Institute for Molecular Science

annual review

2021

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Editorial Committee 2021

Institute for Molecular Science (IMS) is one of the world’s core research facilities for molecular science and is also a center for inter-university joint research in Japan. It sets an extremely wide range of research goals, from understanding the behavior of individual molecules to that of collective molecular systems. These molecular systems have close relation to scientific understanding of biology, engineering and space sciences. Currently, IMS is engaged in six (four plus two) areas of research: Theoretical and computational molecular science, Photo-molecular science, Materials molecular science, and Life and coordination-complex molecular science. Research Center of Integrative Molecular Systems (CIMoS) has started from April 2013 to develop the highly functional molecular systems such as molecular rhythms, sensing and response, and even self-repair. Starting from April 2017, Center for Mesoscopic Sciences (CMS) is launched to develop innovative methodology of studying mesoscopic molecular systems, covering from theoretical methods to leading-edge measurement methods. Division of Advanced Molecular Science is launched to promote outstanding research example of Molecular Science from April 2018. From April 2019, Division of Research Innovation and Collaboration is launched to strengthen the tie between the social activities. In addition to these research divisions, IMS has three research facilities; UVSOR Synchrotron Facility, Instrument Center facilitated with various molecular detectors, and Equipment Development Center. IMS also operates the Research Center for Computational Science, jointly with National Institute for Physiological Sciences and National Institute for Basic Biology in the same campus. From April 2018, Exploratory Research Center on Life and Living Systems (ExCELLS) is launched directly under the National Institutes of Natural Sciences to advance the activity of Okazaki Institute for Integrative Bioscience (OIIB).

Annual Review 2021 is a summary of research activities performed in IMS during September 2020–September 2021. Individual research groups at IMS are making steady progress in basic research on molecular structures, reactions and functions demonstrating “novel molecular capabilities,” as reported in this Review. In addition to these individual activities, IMS conducts the six special programs in the institute basis: (i) Development of cold-atom based quantum simulators and their applications to quantum computing within the framework of Japan’s flagship program on quantum sciences and technologies “Q-LEAP” by MEXT (2018–2028); (ii) Nano science project, called Nanotechnology Platform; (iii) Advanced Research Infrastructure for Materials and Nanotechnology in Japan, from April 2021; (iv) Inter-University Network for Common Utilization of Research Equipments; (v) Project on trans-hierarchical studies of materials and biological systems with molecular observations, as a joint program of NINS; (vi) IMS runs several international collaboration programs and also owns an internship program for young scientists: Institute for Molecular Science International Internship Program (IMS-IIP). IMS-IIP provides the opportunity of internship for young researchers (e.g., master’s and doctoral students, postdoctoral researchers and young faculty members of MOU partners) from overseas to stay in IMS laboratories.

Our life in Okazaki has changed since April 2020 due to the pandemic of COVID19. Utilization of WEB meeting has become the standard for most of the academic meetings and thus the opportunity to meet and discuss with our colleague all around the world has become easier than ever. Unexpecting findings by directly encountering people face to face is no more an everyday life. Accepting Post-Docs and students from outside Japan is extremely difficult. Experimental collaboration based on practical exchange of personal has been restricted, while some new idea to perform the experiment by accepting samples from the users has started this year. From the administration point of view, acceleration of reforming our work style such as work from home has been realized, accompanied with paperless meeting and digitalization of office documents. Such a revolution is still ongoing while the most impressive change was getting rid of our sealing culture in a part.

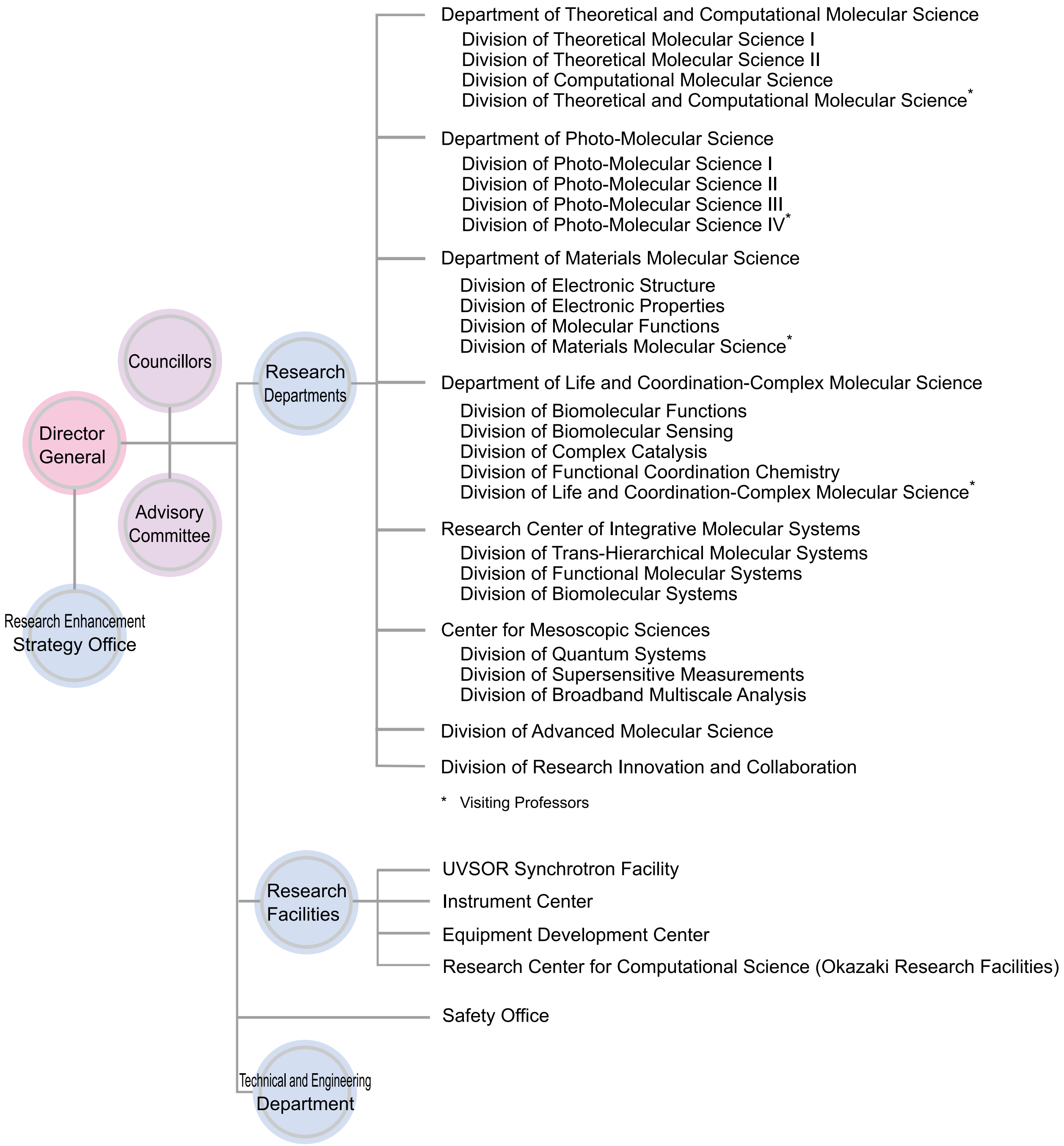
IMS will continue to contribute to lead the Molecular Science together with many young promising and well-established senior scientists. This institute has been most benefited with your constant support and we do expect your further support and advice for creating this new era of molecular science.

August, 2021

Maki Ka

KAWAI, Maki
Director General, Institute for Molecular Science

ORGANIZATION



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      - Division of Theoretical Molecular Science I
      - Division of Theoretical Molecular Science II
      - Division of Computational Molecular Science
      - Division of Theoretical and Computational Molecular Science*
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      - Division of Photo-Molecular Science I
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      - Division of Photo-Molecular Science III
      - Division of Photo-Molecular Science IV*
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      - Division of Electronic Properties
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Professor
p. 10


MINAMITANI, Emi
Associate Professor
p. 12


ISHIZAKI, Akihito
Professor
p. 14


EHARA, Masahiro
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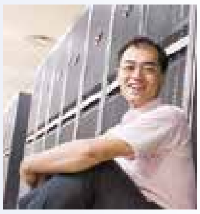
p. 16


OKUMURA, Hisashi
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p. 18


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p. 20


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p. 22

Photo-Molecular Science


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Professor
p. 28


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Professor
p. 30


KATOH, Masahiro
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p. 32


TAIRA, Yoshitaka
Associate Professor
p. 34


TANAKA, Kiyohisa
Associate Professor
p. 36

Materials Molecular Science


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Professor
p. 44


SUGIMOTO, Toshiki
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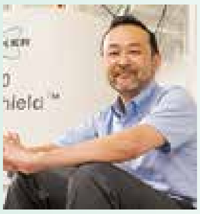
p. 46


HIRAMOTO, Masahiro
Professor
p. 48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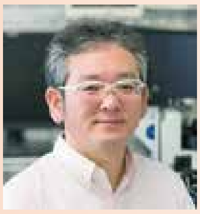
Associate Professor
p. 50


KOBAYASHI, Genki
Associate Professor
p. 52

Life and Coordination-Complex Molecular Science

AONO, Shigetoshi
Professor
p. 58

KATO, Koichi
Professor
p. 60



IINO, Ryota
Professor
p. 62

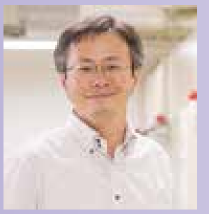
UOZUMI, Yasuhiro
Professor
p. 64

MOMIYAMA, Norie
Associate Professor
p. 66

KUSAMOTO, Tetsuro
Associate Professor
p. 68

SEGAWA, Yasutomo
Associate Professor
p. 70

Research Center of Integrative Molecular Systems



AKIYAMA, Shuji
Professor
p. 74

KOGA, Nobuyasu
Associate Professor
p. 76

KURAMOCHI, Hikaru
Associate Professor
p. 78

YAMAMOTO, Hiroshi
Professor
p. 80

Center for Mesoscopic Sciences

OKAMOTO, Hiromi
Professor
p. 84

KUMAGAI, Takashi
Associate Professor
p. 86

Division of Advanced Molecular Science

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Distinguished
Professor
p. 90

KIMURA, Shin-ichi
Professor
(Cross Appointment)
p. 92

TAKAYA, Hikaru
Associate Professor
(Cross Appointment)
p. 94

Division of Research Innovation and Collaboration

TAIRA, Takunori
Project Professor
p. 98

RESEARCH FACILITIES

UVSOR Synchrotron Facility

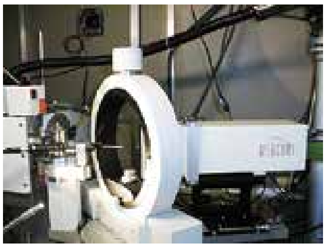
p. 102

KERA, Satoshi
Director

Instrument Center

p. 104

YOKOYAMA, Toshihiko
Director



Equipment Development Center

p. 105

YAMAMOTO, Hiroshi
Director

Research Center for Computational Science (Okazaki Research Facilities)

p. 106

EHARA, Masahiro
Director

PERSONNEL CHANGES

Moving In

Dec. 1, 2020	Res. Assoc. Prof. OKAZAKI, Kei-ichi joined the Department of Theoretical and Computational Molecular Science as an Assoc. Prof.
Jan. 16, 2021	Dr. SATO, Takuro joined IMS as an Assist. Prof. in the Research Center of Integrative Molecular Systems
Feb. 1, 2021	Dr. SUGIYAMA, Haruki joined IMS as an Assist. Prof. in the Department of Life and Coordination-Complex Molecular Science
Feb. 1, 2021	Dr. YONEDA, Yusuke joined IMS as an Assist. Prof. in the Research Center of Integrative Molecular Systems
Apr. 1, 2021	Dr. KUMAGAI, Takashi joined IMS as an Assoc. Prof. in the Center for Mesoscopic Sciences
Apr. 1, 2021	Dr. SUGITA, Kento joined IMS as an Assist. Prof. in the UVSOR Synchrotron Facility
Apr. 1, 2021	Dr. FUKUTANI, Keisuke joined IMS as an Assist. Prof. in the Department of Photo-Molecular Science
Apr. 1, 2021	Dr. NISHIDA, Jun joined IMS as an Assist. Prof. in the Center for Mesoscopic Sciences

Moving Out

Sep. 30, 2020	Assist. Prof. MORI, Toshifumi (Department of Theoretical and Computational Molecular Science) moved out as an Assoc. Prof. of Kyushu University
Mar. 31, 2021	Assist. Prof. IDETA, Shinichiro (UVSOR Synchrotron Facility) moved out as an Assoc. Prof. of Hiroshima University
Mar. 31, 2021	Res. Assoc. Prof. FUJITA, Takatoshi (Department of Theoretical and Computational Molecular Science) moved out to National Institutes for Quantum Science and Technology

ACTIVITIES IN EDUCATION AND COLLABORATION

Graduate Programs

IMS is one of the leading national research institutes in natural science. For graduate education, IMS has two departments in Graduate School of Physical Sciences, SOKENDAI (The Graduate University for Advanced Studies): Department of Structural Molecular Science and Department of Functional Molecular Science. One year is divided into two terms, the first semester (April-to-September) and the second semester (October-to-March).

The graduate education at IMS focuses on the molecular sciences. Each graduate student can study molecular science under guidance of the IMS faculty members in the following areas: Photomolecular science, materials molecular science, biomolecular and coordination molecular science, and theoretical and computational molecular science.

In the 1st and 2nd years of the 5-year doctoral course, the programs emphasize the scientific education related to the expertises of IMS laboratories. By providing such opportunities, the program seeks to help students develop extensive knowledge on physical sciences and high degree of professional quality as well as to help them prepare for the education in their 3rd to 5th years of the 5-year doctoral course.

Young scientists and graduate students from abroad are also encouraged to visit IMS through several opportunities such as the IMS Open Campus and Lecture in June, Summer Training Program in August, and Asian Winter School in addition to IMS International Internship Program as shown below.

International Collaboration and Exchange Programs

Many foreign researchers and students stay for 1–12 months in IMS to collaborate with us in the field of molecular science, or stay for 1–2 weeks to use various kinds of research equipments in our research facilities such as the UVSOR Synchrotron Facility, Instrument Center, and Equipment Development Center. IMS has own budget to carry out these international exchange and collaboration programs, and covers part of research expenses and travel expenses for visitors from abroad. They can use our guest houses, Mishima Lodge and Myodaiji Lodge.

Exchange/Collaboration program		Duration of Stay	Eligibility
IMS visiting faculty program	Long-term	3–12 months	Professors, Associate Professors and other corresponding positions
	Short-term*	1–3 months	
IMS International Internship Program (IMS-IIP)	Long-term	>6 months	Ph.D. students and PostDoc.
	Short-term*	1–6 months	
IMS facility user program		1–2 weeks	Professors, Researchers, and Ph.D. students

* We preferentially invite researchers and students from MOU partnership institutions

International Symposia

We organize several kinds of international symposia based on screening of submitted proposals. In addition, we have international collaborative symposia with MOU partners at IMS or at MOU partner's country as listed in Collaboration Programs.

Program		Purpose
International Symposia and Workshop	Okazaki Conference	An international conference with distinguished foreign researchers by focusing on an emerging field as a fundamental issue in the field of molecular science and related research area
	Mini-International Workshop	A small international workshop on a specific field
	Asia/Oceania IMS Workshop	Workshop with Asian and Oceanian researchers and students
IMS Workshop	IMS Workshop (General)	Workshop on timely topics in molecular science, organized as a collaborative effort between outside and IMS researchers
	IMS Workshop in cooperation with a specified research community	
	IMS Workshop in cooperation with graduate students	Workshop and other related activities planned by graduate students

RESEARCH ACTIVITIES

Theoretical and Computational Molecular Science

The goal of the Department is understanding and prediction of static and dynamic properties, reactions, and functions in condensed phase including biomolecular and heterogeneous catalytic systems by developing novel theories and computational methodologies based on theories in quantum mechanics, statistical mechanics, and solid state physics. The Department collaborates with Research Center for Computational Science on researches.

Theoretical Studies of Reactions, Functions, and Fluctuations in Many-Body Molecular Systems

Department of Theoretical and Computational Molecular Science
Division of Theoretical Molecular Science I

SAITO, Shinji
Professor
[shinji@ims.ac.jp]

Education

1988	B.S. Keio University
1990	M.E. Kyoto University
1995	Ph.D. The Graduate University for Advanced Studies

Professional Employment

1990	Technical staff, Institute for Molecular Science
1994	Research Associate, Nagoya University
1998	Associate Professor, Nagoya University
2005	Professor, Institute for Molecular Science
2006	Professor, The Graduate University for Advanced Studies

Member
Assistant Professor
MORI, Toshifumi*
KODA, Shin-ichi
JSPS Post-Doctoral Fellow
MATSUMURA, Yoshihiro
Post-Doctoral Fellow
MAURYA, Manish†
Graduazte Student
KALATHINGAL, Mahroof
ZHU, Zhe
Secretary
CHIBA, Fumika

Keywords Reactions, Functions, Fluctuations

Many-body molecular systems, such as (supercooled) liquids and biomolecules, exhibit complex fluctuations. Furthermore, in these systems, various physical properties and biological functions are created and chemical reactions proceed under the fluctuations. We aim to elucidate the properties, functions, and reactions by investigating fluctuations and dynamics of the many-body molecular systems.

We have investigated fluctuations and dynamics of liquids by developing computational method for multi-dimensional nonlinear spectroscopy that can reveal detailed dynamical infomation not available from conventional linear spectroscopy. Consequently, we revealed the molecular origins of the ultrafast energy relaxation and time evolution of inhomogeneous fluctuations in liquid water. In supercooled liquids, rare and non-uniform structural changes, called dynamic heterogeneity, are induced by fluctuations. We elucidated the relationship between the lifetime of the dynamic heterogeneity and the fragility using the three-time correlation function of density fluctuations.

We study the molecular origin of anomalous properties of liquid water. We revealed that the anomalies of liquid water are related to the structural and dynamical instabilities hidden in the experimentally inaccessible region and the physical reason of the low glass transition of liquid water. Now we investigate how rare but persistent structural relaxations proceed at low temperatures towards the glass transition temperature.

Complex conformational fluctuations and changes are also found in biomolecular systems. In addition, the conformational dynamics are considered to be essential for biological functions. We examine the relationship between fluctuation and biomolecular function found in the robust circadian rhythm of the clock protein KaiC and the efficient excitation energy transfer in photosynthetic systems. We investigate dynamic effects of enzymatic reactions, and find the importance of prearranged states for the rare but persistent enzymatic reactions. Furthermore, we examine dynamic disorder in conformational changes of proteins at the molecular level.

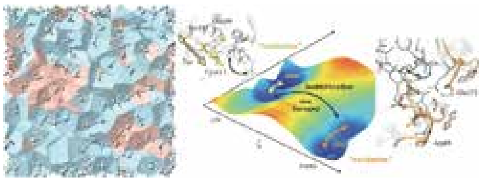


Figure 1. Snapshot of two-state model in supercooled water consisting of high- and low-density liquids (left) and schematic of 2D free energy surface for enzymatic reaction (right).

Selected Publications

- T. Yagasaki and S. Saito, *Annu. Rev. Phys. Chem.* **64**, 55–75 (2013). T. L. C. Jansen, S. Saito, J. Jeon and M. Cho, *J. Chem. Phys.* **150**, 100901 (17 pages) (2019), C. R. Baiz *et al.*, *Chem. Rev.* **120**, 7152–7218 (2020).
- K. Kim and S. Saito, *J. Chem. Phys. (Special Topic on Glass Transition)* **138**, 12A506 (12 pages) (2013).
- S. Saito, B. Bagchi and I. Ohmine, *J. Chem. Phys.* **149**, 124504 (8 pages) (2018), S. Saito and B. Bagchi, *J. Chem. Phys.* **150**, 054502 (14 pages) (2019).
- T. Mori and S. Saito, *J. Phys. Chem. Lett.* **10**, 474–480 (2019).
- S. Saito, M. Higashi and G. R. Fleming, *J. Phys. Chem. B* **123**, 9762–9772 (2019).

1. Molecular Mechanism of Acceleration and Retardation of Collective Orientation Relaxation of Water Molecules in Aqueous Solutions[1)]

The collective orientation relaxation (COR) of water molecules in aqueous solutions is faster or slower with an increase in the concentration of the solutions than that in pure water; for example, acceleration (deceleration) of the COR is observed in a solution of sodium chloride (tetramethyl ammonium chloride) with increasing concentration. However, the molecular mechanism of the solution and concentration dependence of the relaxation time of the COR has not yet been clarified. We theoretically investigate the concentration dependence of the COR of water molecules in solutions of tetramethylammonium chloride (TMACl), guanidinium chloride (GdmCl), and sodium chloride (NaCl). Based on the Mori–Zwanzig equation, we identify two opposing factors that determine the COR of water molecules in any aqueous solution: The correlation of dipole moments and the single-molecule orientation relaxation. We reveal the molecular mechanism of the concentration dependence of the relaxation time of the COR in the TMACl, GdmCl, and NaCl solutions in terms of these two factors.

2. Effects of Interfaces on Structure and Dynamics of Water Droplets on a Graphene Surface: A Molecular Dynamics Study[2)]

The structure and dynamics of water droplets on a bilayer graphene surface are investigated using molecular dynamics simulations. The effects of solid/water and air/water interfaces on the local structure of water droplets are analyzed in terms of the hydrogen bond distribution and tetrahedral order parameter. It is found that the local structure in the core region of a water droplet is similar to that in liquid water. On the other hand, the local structure of water molecules at the solid/water and air/water interfaces, referred to as the interface and surface regions, respectively, consists mainly of three-coordinated molecules that are greatly distorted from a tetrahedral structure. This study reveals that the dynamics in different regions of the water droplets affects the intermolecular vibrational density of states: It is found that in the surface and interface regions, the intensity of vibrational density of states at ~50 cm^{-1} is enhanced, whereas those at ~200 and ~500 cm^{-1} are weakened and redshifted. These changes are attributed to the increase in the number of molecules having fewer hydrogen bonds in the interface and surface regions. Both single-molecule and collective orientation relaxations are also examined. Single-molecule orientation relaxation is found to be marginally slower than that in liquid water. On the other hand, the collective orientation relaxation of water droplets is found to be significantly faster than that of liquid water because of the destructive correlation of dipole moments in the droplets. The negative correlation between distinct dipole moments also yields a blue-shifted libration peak in the absorption spectrum. It is also found that the water–graphene interaction affects the structure and dynamics of the water droplets, such as the local water structure, collective orientation relaxation, and the correlation between dipole moments. This study reveals that the water/solid and water/air interfaces strongly affect the structure and intermolecular dynamics of water droplets and suggests that the intermolecular dynamics, such as energy relaxation dynamics, in other systems with interfaces are different from those in liquid water.

3. Microscopic Insights into Dynamic Disorder in the Isomerization Dynamics of the Protein BPTI[3)]

Understanding the dynamic disorder behind a process, *i.e.*, the dynamic effect of fluctuations that occur on a timescale slower or comparable with the timescale of the process, is essential for elucidating the dynamics and kinetics of complicated molecular processes in biomolecules and liquids. Despite numerous theoretical studies of single-molecule kinetics, our microscopic understanding of dynamic disorder remains limited. In the present study, we investigate the microscopic aspects of dynamic disorder in the isomerization dynamics of the Cys14–Cys38 disulfide bond in the protein bovine pancreatic trypsin inhibitor, which has been observed by nuclear magnetic resonance. We use a theoretical model with a stochastic transition rate coefficient, which is calculated from the 1-ms-long time molecular dynamics trajectory obtained by Shaw *et al.* [*Science* **330**, 341–346 (2010)]. The isomerization dynamics are expressed by the transitions between coarse-grained states consisting of internal states, *i.e.*, conformational sub-states. In this description, the rate for the transition from the coarse-grained states is stochastically modulated due to fluctuations between internal states. We examine the survival probability for the conformational transitions from a coarse-grained state using a theoretical model, which is a good approximation to the directly calculated survival probability. The dynamic disorder changes from a slow modulation limit to a fast modulation limit depending on the aspects of the coarse-grained states. Our analysis of the rate modulations behind the survival probability, in relation to the fluctuations between internal states, reveals the microscopic origin of dynamic disorder.

References

1) N. Moritsugu, T. Nara, S.-i. Koda, K. Tominaga and S. Saito, *J. Phys. Chem. B* **124**, 11730–11737 (2020).
2) M. Manish, A. K. Metya, J. K. Singh and S. Saito, *J. Chem. Phys.* **154**, 164704 (12 pages) (2021).
3) Y. Matsumura and S. Saito, *J. Chem. Phys.* **154**, 224113 (11 pages) (2021).

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† Present Address; University of Alabama

Theoretical Studies on Novel Physical Properties Arising from Many-Body Interaction

Department of Theoretical and Computational Molecular Science
Division of Theoretical Molecular Science I

MINAMITANI, Emi
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[eminamitani@ims.ac.jp]

Education

2005	B.S. Osaka University
2010	Ph.D. Osaka University

Professional Employment

2010	Postdoctoral Fellow, Osaka University
2011	Special Postdoctral Researcher, RIKEN
2013	Assistant Professor, The University of Tokyo
2015	Lecturer, The University of Tokyo
2019	Associate Professor, Institute for Molecular Science Associate Professor, The Graduate University for Advanced Studies

Awards

2008	L'Oréal–UNESCO Japan National Fellowships for Women in Science
2011	Best Poster Award in ISSS-6 Internal Symposium on Surface Science
2017	Young Scientist Award of the Physical Society of Japan
2019	The Commendation for Science and Technology by the Minister of Education, Culture, Sports, Science and Technology The Young Scientists' Prize
2020	The 1st Award for Early Career Women Scientists of the Japan Society of Vacuum and Surface Science
2021	The 2nd Fumiko Yonezawa Memorial Prize of the Physical Society of Japan

Member
Assistant Professor
SHITADE, Atsuo
IMS Research Assistant Professor
MIWA, Kuniyuki
Secretary
AKABA, Atsuko

Keywords Quantum Many-Body Interaction, Density Functional Theory, Quantum Field Theory

Quantum many-body interaction is a source of novel physical properties in the condensed matters. In our group, we develop theoretical methods by combining quantum field theory and density functional theory, and carry out collaborative research with experimental groups. As specific targets, we focus on magnetism in nanostructure and energy dissipation.

For magnetism in nanostructure, we are interested in the Kondo effect and spin–orbit interaction. The Kondo effect arises from the interaction between the localized spin and conduction electrons, which forms a characteristic many-body state so called the Kondo singlet state. The spin–orbit interaction originating from relativistic effect constrains the direction of magnetic moment to specific direction. We investigate the possibility of novel physical phenomena induced by these interactions in the nanostructure and molecules on surfaces.

For energy dissipation, we focus on the effect of electron–phonon interaction. The electron–phonon interaction is one of the most fundamental interactions in the condensed matter physics, and the quantitative evaluation in realistic materials is highly demanding. We adopt the ab-initio calculation to analyze the signal of electron–phonon coupling in surface spectroscopy and thermal properties in various kind of solids.

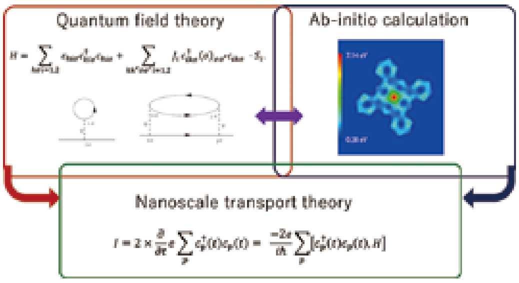

Figure 1. Schematic image of the theoretical method developed in our group.

Selected Publications

- E. Minamitani, N. Tsukahara, D. Matsunaka, Y. Kim, N. Takagi and M. Kawai, "Symmetry-Driven Novel Kondo Effect in a Molecule," *Phys. Rev. Lett.* **109**, 086602 (2012).
- E. Minamitani, R. Arafune, N. Tsukahara, Y. Ohda, S. Watanabe, M. Kawai, H. Ueba and N. Takagi, "Surface Phonon Excitation on Clean Metal Surfaces in Scanning Tunneling Microscopy," *Phys. Rev. B* **93**, 085411 (2016).
- E. Minamitani, N. Takagi and S. Watanabe, "Model Hamiltonian Approach to the Magnetic Anisotropy of Iron Phthalocyanine at Solid Surfaces," *Phys. Rev. B* **94**, 205402 (2016).
- R. Hiraoka, E. Minamitani, R. Arafune, N. Tsukahara, S. Watanabe, M. Kawai and N. Takagi, "Single-Molecule Quantum Dot as a Kondo Simulator," *Nat. Commun.* **8**, 16012 (2017).
- E. Minamitani, R. Arafune, T. Frederiksen, T. Suzuki, S. M. F. Shahed, T. Kobayashi, N. Endo, H. Fukidome, S. Watanabe and T. Komeda, "Atomic-Scale Characterization of the Interfacial Phonon in Graphene/SiC," *Phys. Rev. B* **96**, 155431 (2017).
- E. Minamitani, M. Ogura and S. Watanabe, "Simulating Lattice Thermal Conductivity in Semiconducting Materials Using High-Dimensional Neural Network Potential," *Appl. Phys. Express* **12**, 095001 (2019).

1. Ab Initio Investigation for Initial Process of Joule Heating in Semiconductor

Joule heating in semiconductors is a fundamental problem in solid-state physics. The resulting thermal damage, reduction in operational reliability, and power consumption of nanoscale transistors have become increasingly critical as the device size decreases. The macroscopic definition of the Joule heating is the dot product of the electric field and the current density. The microscopic process of Joule heating in a steady state is described as the energy balance between the electron and phonon intermediated by electron–electron, electron–impurity, electron–phonon, and phonon–phonon interactions under nonequilibrium conditions in the presence of a high electric field. Until recently, the empirical treatment of the band structure and the electron–phonon coupling prevents us from understanding the detail of relaxation process induced by these scattering process quantitatively and microscopically.

We propose a methodology for quantitative investigation of the energy relaxation process with the ab initio treatment of electronic states and electron–phonon interactions by approximating the nonequilibrium electron distribution function as being in equilibrium with an effective temperature.1) This approximation is known as the two-temperature model because the electrons and phonons are described by different effective temperatures, the electron temperature (T_e) and lattice temperature (T_l). The two-temperature model becomes reasonable if the electron equilibration time is sufficiently shorter than the time required for energy relaxation from electrons to phonons. Under such conditions, the Joule heating process can be described by the following three steps: First, electrons accelerated by an electric field are scattered elastically by electron–electron and electron–impurity interactions with a short relaxation time. This process randomizes the electron energy and momentum, and consequently, the electron distribution becomes isotropic in **k**-space, which can be described by a Fermi distribution with T_e. Second, the inelastic electron–phonon scattering with a longer energy relaxation time occurs, and the energy is transferred from the hot electrons to the cold phonons specified by T_l. Finally, the excited phonons are thermalized by the slow phonon–phonon interaction, and the heat energy is radiated to the environment or transported to a thermal bath such as a substrate and/or electrode by thermal phonons. We focus on the second energy transfer process as the initial step of Joule heating and develop a method to evaluate this process based on ab initio calculations.

Recent progress in ab initio calculations by combining density functional theory and the Wannier interpolation technique has enabled the evaluation of electron–phonon coupling with high precision. This technique has been employed to evaluate the transport properties of semiconducting materials. Here, we combine the ab initio calculation of the transport properties with the two-temperature concept. We applied this theoretical approach to bulk Si as a specific target.

As result, we found that the microscopic initial process of Joule heating differed in the electron and hole carriers. Figures 2 (a)–(d) show the phonon dispersion and decomposition of the energy relaxation rates into the contributions from the phonons with <27 meV, <50 meV, and >50 meV energy at low and high T_l as functions of E. The contributions from the phonons with medium energy, the LA and TO modes at the zone boundary, differ for the electron and hole carriers. For the electron carriers, there is a substantial contribution from medium-energy phonons at both low and high T_l. In particular, the relaxation via medium-energy phonons is dominant at low E at low T_l. In contrast, for the hole carriers, the contribution from medium-energy phonons is minor compared to that from the TO and zone center LO modes, except at a very low E at a low T_l. The origin of the differences can be attributed to the presence/absence of the intervalley scattering process and the isotropic/anisotropic band structures in the electron and hole carriers. The important factors that govern the energy relaxation process can be controlled by strain. A detailed ab initio investigation of the energy relaxation rate in a strained structure remains a topic for future research.

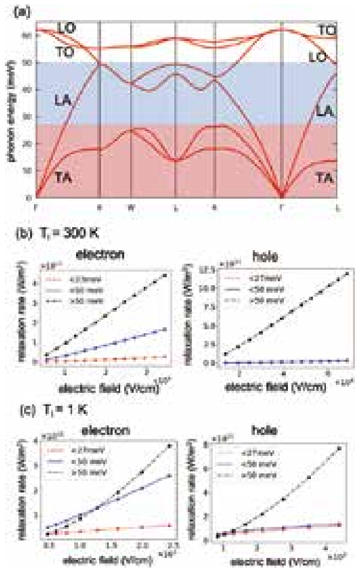

Figure 2. (a) Phonon band structure of bulk Si. The energy relaxation rates of electron and hole carriers are decomposed into contributions from phonons in the three energy ranges at (b) $T_l = 300$ K and (c) $T_l = 1$ K.

2. Other Ongoing Projects:

- Thermal Properties in Amorphous Solids

Reference

1) E. Minamitani, *Phys. Rev. B* **104**, 085202 (2021).

Awards

MINAMITANI, Emi; The 1st Award for Early Career Women Scientists of the Japan Society of Vacuum and Surface Science (2020).
MINAMITANI, Emi; The 2nd Fumiko Yonezawa Memorial Prize of the Physical Society of Japan (2021).
SHITADE, Atsuo; 15th Young Scientist Award of the Physical Society of Japan (2021).
MIWA, Kuniyuki; 15th Young Scientist Award of the Physical Society of Japan (2021).

Theoretical Studies of Chemical Dynamics in Condensed and Biomolecular Systems

Department of Theoretical and Computational Molecular Science Division of Theoretical Molecular Science II

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Education

2001	B.S. Kyoto University
2005	M.S. Kyoto University
2008	D.S. Kyoto University

Professional Employment

2006	JSPS Research Fellow, Kyoto University
2008	JSPS Postdoctoral Fellow for Research Abroad, University of California, Berkeley
2010	Postdoctoral Fellow, Lawrence Berkeley National Laboratory
2012	Research Associate Professor, Institute for Molecular Science
2013	Fellow 2012–2013, Wissenschaftskolleg zu Berlin
2016	Professor, Institute for Molecular Science Professor, The Graduate University for Advanced Studies Visiting professor, Nagoya University

Awards

2015	10th Condensed-Matter Science Prize, Japan
2016	10th Young Scientist Award of the Physical Society of Japan
2016	18th Sir Martin Wood Prize
2017	The Commendation for Science and Technology by the Minister of Education, Culture, Sports, Science and Technology The Young Scientists' Prize
2020	JSPS Prize
2020	Japan Academy Medal

Member
Post-Doctoral Fellow
FUJIHASHI, Yuta
SAKAMOTO, Souichi
JO, Ju-Yeon
Secretary
AKABA, Atsuko

Keywords Quantum Dissipative Systems in Complex Molecular Systems, Quantum Optics, Light-Matter Interaction

Quantum dynamic phenomena are ubiquitous in molecular processes, and yet remain a challenge for experimental and theoretical investigations. On the experimental side, it has become possible to explore molecules on a time scale down to a few femtoseconds. This progress in ultrafast spectroscopy has opened up real-time observation of dynamic processes in complex chemical and biological systems and has provided a strong impetus to theoretical studies of condensed phase quantum dynamics.

Essentially, any quantum systems can never be regarded as "isolated systems." Quantum systems are always in contact with "the outside world," and hence their quantum natures are sometimes sustained and sometimes destroyed. In condensed phase molecular systems, especially, quantum systems are affected by the huge amount of dynamic degrees of freedom such as solvent molecules, amino acid residues in proteins, and so forth. Balance between robustness and fragility of the quantum natures may dramatically alter behaviors of chemical dynamics and spectroscopic signals. Therefore, theoretical tools to adequately describe (1) dynamical behaviors of quantum systems affected by the huge amount of dynamic degrees of freedom and (2) the interaction with radiation fields should be developed.

For this purpose, our research group has been tackling the following subjects:

(1) Developments of condensed phase quantum dynamic theories
(2) Quantum theories to describe dynamical and transport processes in materials and biological systems
(3) Theoretical investigations on measurement and control with the use of atomic-molecular-optical (AMO) physics approaches.

In recent years, specifically, special attention is devoted to the subject (3). We have been examining whether ideas and concepts in the field of quantum science and technology would provide novel control knobs that supplement classical parameters in conventional spectroscopic tools such as frequencies and time delays.

Selected Publications

- A. Ishizaki and G. R. Fleming, "Quantum Coherence in Photosynthetic Light Harvesting," *Annu. Rev. Condens. Matter Phys.* **3**, 333–361 (2012). [Invited review article]
- G. D. Scholes *et al.*, "Using Coherence to Enhance Function in Chemical and Biophysical Systems," *Nature* **543**, 647–656 (2017).
- T. P. Nguyen and A. Ishizaki, "Control of Excitation Energy Transfer in Condensed Phase Molecular Systems by Floquet Engineering," *J. Phys. Chem. Lett.* **9**, 1243 (2018).
- A. Kato and A. Ishizaki, "Non-Markovian Quantum-Classical Ratchet for Ultrafast Long-Range Electron–Hole Separation in Condensed Phases," *Phys. Rev. Lett.* **121**, 647 (2018).
- Y. Fujihashi, R. Shimizu and A. Ishizaki, "Generation of Pseudo-Sunlight via Quantum Entangled Photons and the Interaction with Molecules," *Phys. Rev. Res.* **2**, 023256 (2020).
- A. Ishizaki, "Probing Excited-State Dynamics with Quantum Entangled Photons: Correspondence to Coherent Multidimensional Spectroscopy," *J. Chem. Phys.* **153**, 051102 (2020). [Editor's Pick]

1. Probing Excited-State Dynamics with Quantum Entangled Photons

Quantum light is a key resource for promoting quantum technology. One such class of technology aims to improve the precision of optical measurements using engineered quantum states of light. In this study, we investigate transmission measurement of frequency-entangled broadband photon pairs generated via parametric down-conversion with a monochromatic laser. It is observed that state-to-state dynamics in the system under study are temporally resolved by adjusting the path difference between the entangled twin beams when the entanglement time is sufficiently short. The non-classical photon correlation enables time-resolved spectroscopy with monochromatic pumping. It was further demonstrated that the signal corresponds to the spectral information along anti-diagonal lines of, for example, two-dimensional Fourier-transformed photon echo spectra. This correspondence inspires us to anticipate that more elaborately engineered photon states would broaden the availability of quantum light spectroscopy.1)

2. Achieving Two-Dimensional Optical Spectroscopy with Temporal and Spectral Resolution Using Quantum Entangled Three Photons

Recent advances in techniques for generating quantum light have stimulated research on novel spectroscopic measurements using quantum entangled photons. One such spectroscopy technique utilizes non-classical correlations among entangled photons to enable measurements with enhanced sensitivity and selectivity. In this work, we investigated spectroscopic measurement utilizing entangled three photons generated through cascaded parametric down-conversion. In this measurement, time-resolved entangled photon spectroscopy with monochromatic pumping [A. Ishizaki, *J. Chem. Phys.* **153**, 051102 (2020)] is integrated with the frequency-dispersed two-photon counting technique, which suppresses undesired accidental photon counts in the detector and thus allows one to separate the weak desired signal. This time-resolved frequency-dispersed two-photon counting signal, which is a function of two frequencies, is shown to provide the same information as that of coherent two-dimensional optical spectra. The spectral distribution of the phase-matching function works as a frequency filter to selectively resolve a specific region of the two-dimensional spectra, whereas the excited-state dynamics under investigation are temporally resolved in the time region longer than the entanglement time. The signal is not subject to Fourier limitations on the joint temporal and spectral resolution, and therefore, it is expected to be useful for investigating complex molecular systems in which multiple electronic states are present within a narrow energy range.2)

3. Insights into Photosynthetic Energy Transfer Gained from Free-Energy Structure: Coherent Transport, Incoherent Hopping, and Vibrational Assistance Revisited

Giant strides in ultrashort laser pulse technology have enabled real-time observation of dynamical processes in complex molecular systems. Specifically, the discovery of oscillatory transients in the two-dimensional electronic spectra of photosynthetic systems [G. S. Engel, *et al.*, *Nature* **446**, 782 (2007)] stimulated a number of theoretical investigations exploring the possible physical mechanisms of the remarkable quantum efficiency of light harvesting processes. In this work, we revisited the elementary aspects of environment-induced fluctuations in the involved electronic energies and present a simple way to understand energy flow with the intuitive picture of relaxation in a funnel-type free-energy landscape. The presented free-energy description of energy transfer reveals that typical photosynthetic systems operate in an almost barrierless regime. The approach also provides insights into the distinction between coherent and incoherent energy transfer and the criteria by which the necessity of the vibrational assistance is considered.3)

4. Direct and Ultrafast Probing of Quantum Many-Body Interaction and Mott-Insulator Transition through Coherent Two-Dimensional Spectroscopy

Interactions between particles in quantum many-body systems play a crucial role in determining the electric, magnetic, optical, and thermal properties of the system. The recent progress in the laser-pulse technique has enabled the manipulations and measurements of physical properties on ultrafast timescales. In this work, we proposed a method for the direct and ultrafast probing of quantum many-body interaction through coherent two-dimensional (2D) spectroscopy. Up to a moderate interaction strength, the inter-particle interaction manifests itself in the emergence of off-diagonal peaks in the 2D spectrum before all the peaks coalesce into a single diagonal peak as the system approaches the Mott-insulating phase in the strongly interacting regime. The evolution of the 2D spectrum as a function of the time delay between the second and third laser pulses can provide important information on the ultrafast time variation of the interaction.4)

References

1) A. Ishizaki, *J. Chem. Phys.* **153**, 051102 (7 pages) (2020). [Editor's Pick]
2) F. Fujihashi and A. Ishizaki, *J. Chem. Phys.* **155**, 044101 (13 pages) (2021).
3) A. Ishizaki and G. R. Fleming, *J. Phys. Chem. B* **125**, 3286–3295 (2021).
4) T. P. Nguyen and Q. T. Pham, *arXiv:*2009.08598 (2021).

Awards

FUJIHASHI, Yuta; 15th Young Scientist Award of the Physical Society of Japan (2021).
ISHIZAKI, Akihito; Research Award of Quantum Life Science Society (2021).

Theoretical Studies of Functional Molecular Systems and Heterogeneous Catalysts

Department of Theoretical and Computational Molecular Science
Division of Computational Molecular Science

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Professor
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Education

1988	B.E. Kyoto University
1990	M.E. Kyoto University
1993	Ph.D. Kyoto University

Professional Employment

1993	Postdoctral Fellow, Institute for Fundamental Chemistry
1994	JSPS Postdoctoral Fellow
1994	Visiting Researcher, Heidelberg University (–1995)
1995	Assistant Professor, Kyoto University
2002	Associate Professor, Kyoto University
2006	Theoretical Research Division Supervisor, Kyoto University (–2008)
2008	Professor, Institute for Molecular Science Professor, The Graduate University for Advanced Studies
2012	Professor, Elements Strategy Initiative for Catalysts and Batteries (ESICB), Kyoto University (additional post)

Awards

2009	APATCC Pople Medal
2009	QSCP Prize CMOA

Member

Post-Doctoral Fellow
- ZHAO, Pei
- KANAZAWA, Yuki

Graduate Student
- SAKUMA, Koya
- HATORI, Atsuya

Secretary
- SUGIMOTO, Yukari

Keywords Quantum Chemistry, Photophysical Chemistry, Heterogeneous Catalysis

We develop the accurate electronic structure theories and investigate the photochemistry and catalysis theoretically. Currently, our focuses are following research subjects.

(1) Coupled cluster theory for excited states of large system

We develop the coupled cluster theories and their efficient computational algorithm aiming at large-scale calculations of molecular excited states. We also develop the basic theories and methodologies that are useful for fundamental chemistry and applied chemistry; for example, PCM SAC-CI method for effectively describing the solvent effects on excited states, CAP/SAC-CI method for locating metastable resonance states, general-R method for multiple excited states, and active-space method for efficiently describing complex electronic states.

(2) Heterogeneous catalysis

Metal nanoclusters supported by metal oxides or polymers achieve highly efficient catalytic reactions. We study the catalytic activity of these complex systems by means of quantum chemical calculations and informatics theories. We have elucidated the importance of the perimeter sites at heterojunction of Ag nanocluster supported by alumina surface in terms of H_2 activation, the mechanism of methanol oxidation on Au:PVP and the unique coupling reactions on Au/Pd:PVP. We proceed these works in the project of Elements Strategy Initiative for Catalysts and Batteries (ESICB).

(3) Photophysical chemistry

Our accurate electronic structure theories are applied to wide varieties of theoretical studies and sometimes in cooperation with experiments on the photophysical properties and excited-state dynamics of nano-bio systems like photo-electronic devices, photofunctional molecules, and biosensors. Target molecules include nanocarbons like fullerenes, near-IR absorbing phthalocyanine congeners, dye-sensitized solar cells, organometallic compounds for artificial photosynthesis, biological chemosensors, and bio-imaging probes.

(4) Theoretical spectroscopy

New quantum states, single-site and two-site double-core hole states, have been observed owing to the recent development of free electron laser and coincidence spectroscopy. We have proposed new chemical concept regarding the physical properties or relaxation processes of these quantum states in cooperation with experiments. We also perform accurate theoretical analysis for the state-of-the-art molecular spectroscopy; for example, the electronic transitions in the FUV region by ATR-FUV spectroscopy and the excited-state relaxation processes by pump–probe spectroscopy.

Selected Publications

- R. Cammi, R. Fukuda, M. Ehara and H. Nakatsuji, "SAC-CI Method in the Polarizable Continuum Model-Theory for Solvent Effect on Electronic Excitation of Molecules in Solution," *J. Chem. Phys.* **133**, 024104 (24 pages) (2010).
- N. Berrah, M. Tashiro, M. Ehara *et al.*, "Double Core-Hole Spectroscopy for Chemical Analysis with an Intense X-Ray Femtosecond Laser," *Proc. Natl. Acad. Sci. U.S.A.* **108**, 16912–16915 (2011).
- M. Ehara and T. Sommerfeld, "CAP/SAC-CI Method for Calculating Resonance States of Metastable Anions," *Chem. Phys. Lett.* **537**, 107–112 (2012).
- P. Hirunsit, K. Shimizu, R. Fukuda, S. Namuangruk, Y. Morikawa and M. Ehara, "Cooperative H_2 Activation at Ag Cluster/θ-Al_2O_3 Dual Perimeter Sites: A DFT Study," *J. Phys. Chem. C* **118**, 7996–8006 (2014).

1. Mechanistic Studies on Photoinduced Catalytic Olefin Migration Reactions at the Pd(II) Centers of a Porous Crystal, Metal-Macrocycle Framework[1)]

Porous crystals with well-defined active metal centers on the pore surface have high potential as heterogeneous metal catalysts. We have recently demonstrated that a porous molecular crystal, metal-macrocycle framework (MMF), catalyzes olefin migration reactions by photoactivation of its $Pd^{II}Cl_2$ moieties exposed on the crystalline channel surface. Herein we report a mechanistic study of the photoinduced olefin migration reactions at the Pd^{II} active centers of MMF. Several experiments, including a deuterium scrambling study, revealed that olefin migration is catalyzed *via* an alkyl mechanism by *in situ* generated Pd-H species on the channel surface during photoirradiation. This proposed mechanism was further supported by DFT and ONIOM calculations.

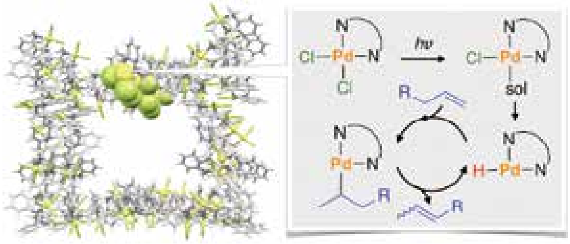

Figure 1. Porous Crystal Metal-Macrocyclic Framework show characteristic photoinduced olefin migration reaction at the Pd^{II} active centers.

2. Selective Catalytic Reduction of NO with NH_3 over Cu-Exchanged CHA, GME, and AFX Zeolites: A Density Functional Theory Study[2)]

Density functional theory calculations have been applied to study the selective catalytic reduction of NO by NH_3 over the Cu-exchanged zeolites with *cha*, *gme*, and *aft* cages. The Cu^I, Cu^{II}, and $[Cu^{II}(OH)]^+$ ions are considered as the active sites to study both the reduction and oxidation processes during the catalytic cycle. In the case of the reduction process, the NH_2NO formation at the $[Cu^{II}(OH)]^+$ site possesses high barriers in the three frameworks, while the lower barriers are found at the Cu^{II} site. Importantly, it is found that the barriers are largely decreased at the solvated $[Cu^{II}(NH_3)_4]^{2+}$ site for the *cha* and *aft* frameworks, while the barrier is only slightly decreased for the *gme* cage. As for the oxidation, the nitrate formation has similar reaction barriers at the Cu^I site of the three frameworks, which are lower than the following nitrite formation. In particular, the smallest *gme* cage possesses the highest barrier for the nitrite formation. Calculations on the O_2 activation by the NH_3-solvated Cu dimer revealed that the *cha* and *aft* cages have better performance than the *gme* cage, and the much smaller adsorption energy of O_2 in the *gme* cage indicates the unfavorable O_2 insertion. Therefore, the selectivity caused by the cage size is identified during the reaction process, and the *cha* and *aft* cages are more favorable.

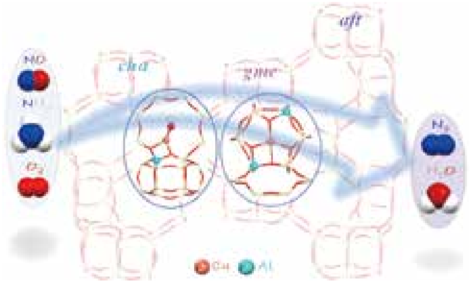

Figure 2. Density functional theory calculations on selective catalytic reduction of NO by NH_3 over the Cu-exchanged zeolites with *cha*, *gme*, and *aft* cages revealed the selectivity caused by the cage size during the reaction process.

3. Facet-Dependent Catalytic Activity of Anatase TiO_2 for the Selective Catalytic Reduction of NO with NH_3: A Dispersion-Corrected Density Functional Theory Study[3)]

Recently, the facet-dependent catalytic activity of anatase TiO_2 for the selective catalytic reduction of NO with NH_3 (NH_3-SCR) has been observed experimentally. In this study, the NH_3-SCR of NO on the TiO_2 (001) and (101) surfaces was systematically investigated using dispersion-corrected density functional theory. We propose that the surface-assisted mechanism is predominant on the (001) surface, which involves the oxygen active sites playing a crucial role in facilitating the reaction. The NH_3 dissociation step reveals the largest activation energy barrier (E_a) of 61 kJ/mol on the (001) surface, whereas the NH_2NO decomposition step has the largest barrier, $E_a \approx 156$ kJ/mol, on the (101) surface. The results obtained by calculation are consistent with the experimental results, which have shown that a TiO_2 nanosheet with a dominant (001) facet shows superior catalytic performance in NH_3-SCR of NO compared to TiO_2 nanoparticles with dominant (101) facet.

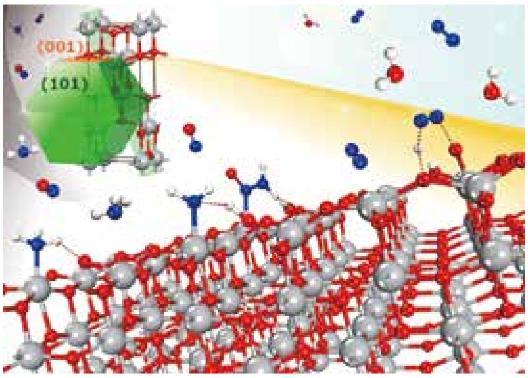

Figure 3. NH_3-SCR of NO on the (001) facet of anatase TiO_2.

References

1) H. Yonezawa, T. Shiraogawa, M. Han, S. Tashiro, M. Ehara and M. Shionoya, *Chem. –Asian J.* **16**, 202–206 (2021).

2) P. Zhao, B. Boekfa, K. Shimizu, M. Ogura and M. Ehara, *Catal. Sci. Technol.* **11**, 1780–1790 (2021).

3) A. Junkaew, M. Ehara, L. Huang and S. Namuangruk, *Appl. Catal., A* **623**, 118250 (2021).

Molecular Dynamics Simulations of Disease-Related Biomolecules

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Division of Computational Molecular Science

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Education

1998	B.S. Keio University
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Professional Employment

2002	Postdoctoral Fellow, The University of Tokyo
2002	Research Associate, Institute for Molecular Science
2004	Research Associate, The Graduate University for Advanced Studies
2006	Research Lecturer, Nagoya University
2008	Research Assistant, Rutgers University
2009	Assistant Research Professor, Rutgers University
2009	Associate Professor, Institute for Molecular Science Associate Professor, The Graduate University for Advanced Studies
2018	Associate Professor, Exploratory Research Center on Life and Living Systems (ExCELLS)

Award

2014	Academic Award of the Molecular Simulation Society of Japan

Member
Assistant Professor
ITOH, Satoru G.
Post-Doctoral Fellow
TANIMOTO, Shoichi
Graduate Student
YAMAUCHI, Masataka
MIYAZAWA, Kazuhisa
FUKUHARA, Daiki
Secretary
KAWAGUCHI, Ritsuko

Keywords Molecular Dynamics Simulation, Protein, Amyloid

Biomolecules such as proteins and peptides have complicated free-energy landscape with many local minima. The conventional canonical-ensemble molecular dynamics (MD) simulations tend to get trapped in a few of the local-minimum states. To overcome these difficulties, we have proposed new generalized-ensemble algorithms, such as replica-permutation method. We apply these methods to proteins and peptides and try to predict the native structures of proteins as in Figure 1.

We are also interested in disease-related biomolecules. For example, protein aggregates such as spherical substances called oligomers and acicular substances called amyloid fibrils (Figure 2) cause more than 30 kinds of diseases. Alzheimer's disease is thought to be caused by aggregated amyloid-β (Aβ) peptides. To overcome these diseases, it is essential to understand the aggregate genesis and disruption of Aβ peptides. We perform such MD simulations of oligomers and amyloid fibrils.

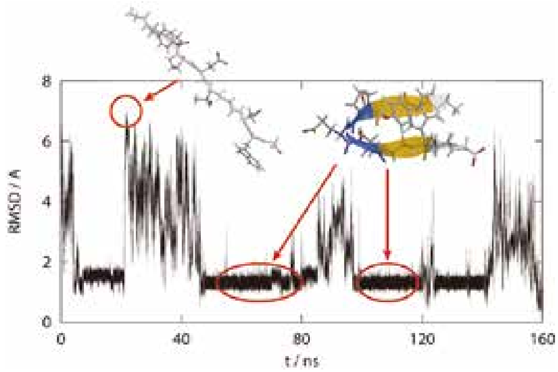

Figure 1. Time series of protein folding simulation.

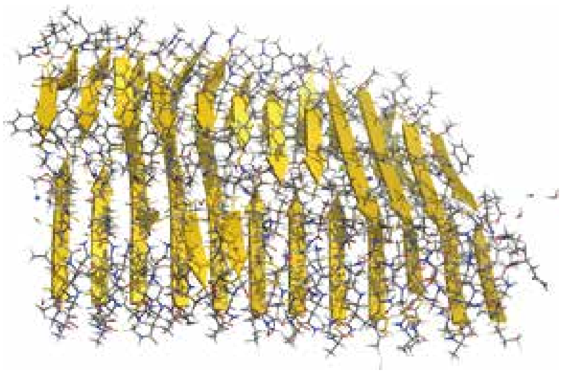

Figure 2. Snapshot of an Aβ amyloid fibril.

Selected Publications

- H. Okumura and S. G. Itoh, "Amyloid Fibril Disruption by Ultrasonic Cavitation: Nonequilibrium Molecular Dynamics Simulations," *J. Am. Chem. Soc.* **136**, 10549–10552 (2014).
- H. Okumura and S. G. Itoh, "Structural and Fluctuational Difference between Two Ends of Aβ Amyloid Fibril: MD Simulation Predicts Only One End Has Open Conformations," *Sci. Rep.* **6**, 38422 (9 pages) (2016).
- S. G. Itoh and H. Okumura, "Replica-Permutation Method with the Suwa-Todo Algorithm beyond the Replica-Exchange Method," *J. Chem. Theory Comput.* **9**, 570–581 (2013).
- S. G. Itoh and H. Okumura, "Oligomer Formation of Amyloid-β(29-42) from Its Monomers Using the Hamiltonian Replica-Permutation Molecular Dynamics Simulation," *J. Phys. Chem. B* **120**, 6555–6561 (2016).

1. Role of Water Molecules in the Laser-Induced Disruption of Amyloid Fibrils Observed by Nonequilibrium Molecular Dynamics Simulations

Water plays a crucial role in the formation and destruction of biomolecular structures. The mechanism for destroying biomolecular structures was thought to be an active breaking of hydrogen bonds by water molecules. However, using non-equilibrium molecular dynamics simulations, in which an Aβ amyloid fibril was destroyed via infrared free-electron laser (IR-FEL) irradiation, we discovered a new mechanism, in which water molecules disrupt protein aggregates,[1] as shown in Figure 3. The intermolecular hydrogen bonds formed by C=O and N–H in the fibril are broken at each pulse of laser irradiation. These bonds usually spontaneously reform after the irradiation in many cases. However, when a water molecule happens to enter the gap between C=O and N–H, it inhibits the reformation of the hydrogen bonds. Such sites become defects in the regularly aligned hydrogen bonds, from which all hydrogen bonds in the intermolecular β-sheet are broken as the fraying spreads. This role of water molecules is entirely different from other known mechanisms. This new mechanism can explain the recent experiments showing that the amyloid fibrils are not destroyed by laser irradiation under dry conditions. Additionally, we found that helix structures form more after the amyloid disruption; this is because the resonance frequency is different in a helix structure. Our findings provide a theoretical basis for the application of IR-FEL to the future treatment of amyloidosis.

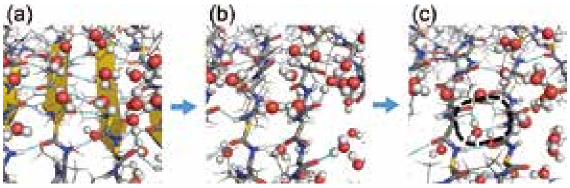

Figure 3. Snapshots of the disruption process of the hydrogen bonds between the Aβ peptides. (a) Hydrogen bonds are formed between Aβ peptides. (b) These hydrogen bonds are broken by the IR-FEL. (c) Water molecule enters the gap between C=O and N–H, it inhibits the reformation of the hydrogen bonds.

2. Replica-Permutation Molecular Dynamics Simulations of an Amyloid-β(16–22) Peptide and Polyphenols

Polyphenols are known to inhibit the aggregation of Aβ peptides. We performed all-atom replica-permutation molecular dynamics simulations of an Aβ fragment, $A\beta_{16-22}$, and two kinds of polyphenols, myricetin and rosmarinic acid in explicit water solvent.[2] We found that glutamic acid E22 of the $A\beta_{16-22}$ peptide has the highest probability to bind to the polyphenols and specified the hydroxyl groups and carboxyl groups of polyphenols that contribute to the binding.

3. "Bucket Brigade" Using Lysine Residues in RNA-Dependent RNA Polymerase of SARS-CoV-2

The RNA-dependent RNA polymerase (RdRp) of severe acute respiratory syndrome coronavirus 2 (SARS-CoV-2) is a promising drug target for coronavirus disease 2019 (COVID-19) because it plays the most important role in the replication of the RNA genome. Nucleotide analogs such as remdesivir and favipiravir are thought to interfere with the RNA replication by RdRp. More specifically, they are expected to compete with nucleoside triphosphates, such as adenosine triphosphate (ATP). However, the process in which these drug candidates and nucleoside triphosphates are taken up by RdRp remains unknown. We performed all-atom molecular dynamics simulations to clarify the recognition mechanism of RdRp for these drug candidates and ATP that were at a distance.[3] The ligand recognition ability of RdRp decreased in the order of remdesivir, favipiravir, and ATP. We also identified six recognition paths. Three of them were commonly found in all ligands, and the remaining three paths were ligand-dependent ones. In the common two paths, it was observed that the multiple lysine residues of RdRp carried the ligands to the binding site like a "bucket brigade," as shown in Figure 4. In the remaining common path, the ligands directly reached the binding site. Our findings contribute to the understanding of the efficient ligand recognition by RdRp at the atomic level.

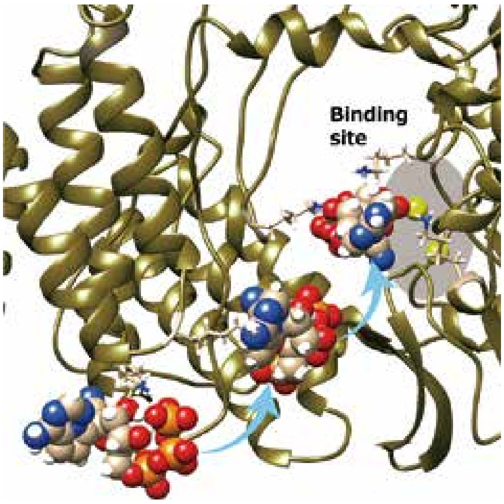

Figure 4. Remdesivir (shown in the sphere model) is transferred to two Mg^{2+} ions (yellow-green spheres) at the binding site of the RNA polymerase while being passed from one lysine residue (shown in the stick model) to another.

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Functional Dynamics of Biomolecular Machines Revealed by Theoretical Methods

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Keywords Theoretical Biophysics, Biomolecular Machines, Molecular Motors

Biomolecular machines, such as molecular motors and transporters in the cell, are known to change their structure when they function. For example, ATP synthase, which synthesizes ATP in mitochondria, is a molecular motor that uses chemical energy to rotate. Transporters, which transport substrate molecules across the cell membrane, perform substrate transport by changing their structure between an inwardly and outwardly open structure relative to the membrane. Our goal is to elucidate the mechanism of these elaborate and dynamic nanomachines created by nature at the atomic and molecular level, and to control their functions based on our findings.

We would like to understand the mechanism of biomolecular machines by "seeing" the motion of biomolecular machines at the moment they function, on a computer at the molecular level. However, this is not an easy task, because biomolecular machines are huge molecules, and their functioning time scale is slow (for a molecular scale) at milliseconds or longer. Conventional atomistic molecular dynamics (MD) simulations cannot cover millisecond-long functional dynamics, especially for a large system like typical biomolecular machines. Therefore, we are trying to capture the motion at the moment of function by using methods such as an importance sampling technique, or coarse-graining multiple atoms together.

We have been working on biomolecular motors such as ATP synthase. ATP synthase is a rotary motor that produces most of ATP required in the cell. It is composed of two rotary motors: $\mathrm{F_o}$ and $\mathrm{F_1}$. $\mathrm{F_o}$ motor is embedded in the membrane driven by proton gradient, while $\mathrm{F_1}$ motor is driven by ATP hydrolysis reaction. We clarified how the rotation of $\mathrm{F_1}$ motor is driven by a key chemical step, $\mathrm{P_i}$ release after ATP hydrolysis reaction, by accelerating atomistic MD simulations with external forces.

Transporters are membrane proteins that transport their substrates across the membrane. We have studied $\mathrm{Na^+/H^+}$ antiporter that exchanges sodium ions and protons inside and outside the cell. The ion transport by the $\mathrm{Na^+/H^+}$ antiporter was simulated in atomic detail with the transition path sampling technique to capture the moment of the ion transports. The simulations predicted the mutation that can speed up the ion transport. The mutation was tested in experiments and shown to speed up the ion transport twice faster than the wild type. Therefore, we succeeded in controlling the function of the transporter based on mechanism obtained from simulations.

Selected Publications

- K. Okazaki and G. Hummer, "Phosphate Release Coupled to Rotary Motion of $\mathrm{F_1}$-ATPase," *Proc. Natl. Acad. Sci. U.S.A.* **110**, 16468–16473 (2013).
- K. Okazaki and G. Hummer, "Elasticity, Friction, and Pathway of γ-Subunit Rotation in $\mathrm{F_oF_1}$-ATP Synthase," *Proc. Natl. Acad. Sci. U.S.A.* **112**, 10720–10725 (2015).
- K. Okazaki, D. Wöhlert, J. Warnau, H. Jung, Ö. Yildiz, W. Kühlbrandt and G. Hummer, "Mechanism of the Electroneutral Sodium/Proton Antiporter PaNhaP from Transition-Path Shooting," *Nat. Commun.* **10**, 1742 (2019).

1. Mechanism of Unidirectional Motions of Chitinase

Processive cellulase and chitinase recently have been cast new light as a different type of biomolecular motors that use hydrolysis energy of polysaccharides for their unidirectional movements. We used single-molecule trajectories to estimate an underlying diffusion model with chemical-state-dependent free energy profile.1) To consider nonequilibrium trajectories driven by the chemical energy consumed by biomolecular motors, we developed a novel framework based on a hidden Markov model, wherein switching among multiple energy profiles occurs reflecting the chemical state changes in motors. The chemical-state-dependent free energy profile underlying the burnt-bridge Brownian ratchet mechanism of processive chitinase was determined.1)

2. Mechanism of Na^+/H^+ Antiporter and Engineering of a Faster Transporter

Na^+/H^+ antiporters control pH and Na^+ concentration in the cell by exchanging sodium ions and protons across lipid membranes. They belong to the cation/proton antiporter (CPA) superfamily, and prevail in all domains of life. The archaeal Na^+/H^+ antiporters PaNhaP from *Pyrococcus abyssi* and MjNhaP1 from *Methanocaldococcus jannaschii* as well as human NHE1, which is linked to a wide spectrum of diseases from heart failure to autism and has no structure solved yet, are electroneutral antiporters of the CPA1 family, exchanging one proton against one sodium ion. As a model system in mechanistic studies of electroneutral Na^+/H^+ exchange, we studied the transport mechanism of PaNhaP.2)

Na^+/H^+ antiporters use the gradient of either sodium ion or proton to drive the uphill transport of the other ion (Figure 1A). The conformational transition of the transporter makes the ion-binding site accessible from either side of the membrane in the alternating manner. For PaNhaP, the inward-open conformation was obtained by X-ray crystallography, while the outward-open conformation is not known experimentally. We modelled the outward-open conformation by MDFF flexible fitting to the low-resolution outward-open structure of the homologous MjNhaP1 from cryo-EM, followed by the long equilibrium MD simulations. It was shown that the transporter domain moves ~3.5 Å in the direction normal to the membrane to take the outward-open state.

By applying the transition path sampling technique, we sampled unbiased transition paths between the inward- and outward-open states. In analysis of the transition paths, we found hydrophobic gates above and below the ion-binding site, which open and close in response to the domain motions (Figure 1B). From the reaction coordinate analysis, it was shown that open-close motion of the outside gate (Ile163-Tyr255) is a rate-limiting step of the alternating-access conformational change. Based on this result, we weakened the outside gate by mutating the residues to both alanine. It was expected that this mutation lowers the barrier and makes the ion transport faster. It was confirmed by experiments that the ion-transport speed of the mutant is indeed twice faster than the wild-type transporter.

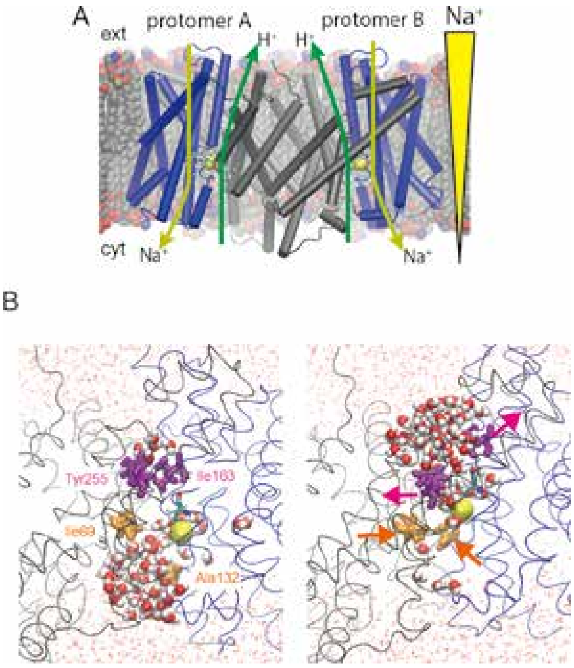

Figure 1. (A) PaNhaP dimer structure. (B) The outside (purple) and inside (orange) gates found in the transition path simulations.

3. Mechanism of Membrane Remodeling by F-BAR Protein Pacsin1

F-Bin/Amphiphysin/Rvs (F-BAR) domain proteins play essential roles in biological processes that involve membrane remodelling, such as endocytosis and exocytosis. Notably, Pacsin1 from the Pacsin/Syndapin subfamily has the ability to transform the membrane into various morphologies: striated tubes, featureless wide and thin tubes, and pearling vesicles. We clarified the membrane curvature induction and sensing characteristics of Pacsin1 by combining all-atom (AA) and coarse-grained (CG) MD simulations.3) By matching structural fluctuations between AA and CG simulations, a CG protein model called "Gō-MARTINI" was developed and optimized.4) The model should prove useful for describing protein dynamics that are involved in membrane remodeling processes.

References

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2) K. Okazaki, D. Wöhlert, J. Warnau, H. Jung, Ö. Yildiz, W. Kühlbrandt and G. Hummer, *Nat. Commun.* **10**, 1742 (2019).
3) M. I. Mahmood, H. Noguchi and K. Okazaki, *Sci. Rep.* **9**, 14557 (2019).
4) M. I. Mahmood, A. B. Poma and K. Okazaki, *Front. Mol. Biosci.* **8**, 619381 (2021).

Theoretical Studies on Molecular Aggregates

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2011	JSPS Postdoctoral Fellow (PD)
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2015	Postdoctral Fellow, Kyoto University
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2021	Senior Researcher, National Institutes for Quantum Science and Technology

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Keywords Exciton, Energy and Charge Transfer, Organic Semiconductors

Organic molecules can assemble into an ordered structure by non-covalent interactions, forming various types of aggregates. Molecular aggregates can exhibit remarkable optical and electronic properties that are not observed in isolated molecules. We study optoelectronic properties and quantum dynamics of molecular aggregates. More specifically, we focus on energy and charge transfer dynamics, energy conversions, and structure-property relationship. Our research also include the developments of theoretical and computational methods.

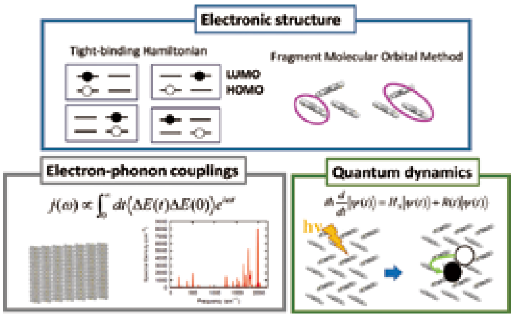

Figure 1. A combine approach to quantum dynamics in molecular aggregates.

It is still challenging to simulate quantum dynamics of energy or charge transfer in condensed systems. An exciton or electron wave functions can be delocalized over many molecules by intermolecular electronic couplings. By contrast, the wave functions can be localized because of the static disorder and interactions with nuclear degree of freedom. Therefore, successful theoretical descriptions require the inclusions of electronic couplings, static disorder, and electron–phonon or electron–vibration interaction. We develop a method to simulate quantum dynamics in condensed phase by combining molecular dynamics simulations, electronic structure theories, and quantum dynamics methods, as shown in Figure 1. Electronic states of an aggregate are obtained from a large-scale electronic structure calculation, and the model Hamiltonian for an exciton or a charge carrier is derived. The model Hamiltonian is used for simulating energy or charge dynamics by a quantum dynamics method, which incorporates finite-temperature effects and electron–vibration interactions. The combined computational approach allows for bottom-up descriptions of energy or charge transfer dynamics in realistic molecular aggregates.

We currently investigate electronic states and quantum dynamics at organic interfaces. We also develop the many-body perturbation theory to predict electronic levels at higher accuracy.

Selected Publications

- T. Fujita, S. Atahan-Evrenk, N. P. D. Sawaya and A. Aspuru-Guzik, "Coherent Dynamics of Mixed Frenkel and Charge Transfer Excitons in Dinaphtho[2,3-*b*:2'3'-*f*]thieno[3,2-*b*]-thiophene Thin Films: The Importance of Hole Delocalization," *J. Phys. Chem. Lett.* 7, 1374–1380 (2016).
- T. Fujita and Y. Mochizuki, "Development of the Fragment Molecular Orbital Method for Calculating Nonlocal Excitations in Large Molecular Systems," *J. Phys. Chem. A* **122**, 3886–3898 (2018).

1. Fragment-Based Excited-State Calculations Using the GW Approximation and Bethe–Salpeter Equation(1)

Accurate calculations of electronic states are essential for the computational studies of organic semiconductor materials, toward understanding of electronic processes in organic devices. The electronic processes in organic electronic devices, such as charge injection and electron–hole separation, are governed by the energies of the charged and neutral excited states. Although the Kohn–Sham (KS) density functional theory (DFT) has been established to be accurate for investigating the ground-state properties, a more sophisticated method is required for excited states. The many-body Green's function method within the GW approximation has been established as a standard approach for the first-principle computation of the charged excitations in condensed matter. Further, neutral excited states can be computed using the Bethe–Salpeter equation (BSE) within the GW approximation, *i.e.*, the GW/BSE method. In particular, the GW/BSE method can yield the correct long-range asymptotic behaviors of the charge-transfer excited states in both gas and condensed phases, which is in contrast to the standard time-dependent DFT.

In this study, we present a fragment-based approach for calculating the charged and neutral excited states in molecular systems, based on the many-body Green's function method within the GW approximation and Bethe–Salpeter equation. Our implementation relies on the many-body expansion of the total irreducible polarizability in the basis of fragment molecular orbitals. The GW quasiparticle energies in complex molecular environments are obtained by the GW calculation for the target fragment plus induced polarization contributions of the surrounding fragments at the static Coulomb-hole plus screened exchange level. In addition, we develop a large-scale GW/BSE method for calculating the delocalized excited states of molecular aggregates, based on the fragment molecular orbital method and the exciton model. The accuracy of fragment-based GW and GW/BSE methods were evaluated on the molecular clusters and molecular crystal. We found that the accuracy of the total irreducible polarizability can be improved systematically by including two-body correction terms, and the fragment-based calculations can reasonably reproduce the results of the corresponding unfragmented calculations with a relative error of less than 100 meV. The proposed approach enables the efficient excited-state calculations for large molecular systems with reasonable accuracy.

2. Excited-State Dynamics Based on the FMO and Wavepacket Propagation Method(2)

We develop a method to investigate the excited-state dynamics in organic molecular aggregates. Our approach is based on three components: (i) FMO-based electronic coupling calculations, (ii) derivations of model Hamiltonians, and (iii) a wavepacket dynamics method. Using the electronic couplings obtained from an FMO calculation for an aggregate, we derive a model Hamiltonian that describes a charge carrier or an exciton in the aggregate. From a theoretical viewpoint, an ab initio many-electron Hamiltonian can be mapped into a reduced one-body or two-body Hamiltonian through the FMO calculation. The time evolution of the model Hamiltonian is then simulated using a wavepacket propagation method. We attempt to understand photophysical and optoelectronic processes in a molecular aggregate as the quasiparticle dynamics described by the model Hamiltonian. We have implemented the electronic coupling calculations and model Hamiltonian derivations into the ABINIT-MP program. In view of computations, an FMO calculation by the ABINIT-MP program provides Hamiltonian matrix elements. The matrix data are then passed to other software that simulates the time propagation.

We investigated the excited-state dynamics in the DNTT thin film and the C_{60}/pentacene (PEN) interface. In particular, we highlight the spatial extents of the electron and hole wave functions that constitute exciton states. We show that the dynamics of the electron and hole wave functions play essential roles in optoelectronic processes, such as the exciton relaxation dynamics and charge separation. Because the extent of delocalization is determined by the interplay among electronic couplings, structural disorder, and finite-temperature effects, the combined approach based on the FMO and wavepacket dynamics is indispensable. Although we have focused on the organic materials, our approach is general and can be applied to other molecular systems. Potential applications include functional supramolecular systems and bio-inspired materials, as well as organic electronic materials.

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2) T. Fujita and T. Hoshi, *Recent Advances of the Fragment Molecular Orbital Method*, Y. Mochizuki, S. Tanaka and K. Fukuzawa, Eds., Springer; Singapore, pp. 547–566. (2021).

Theory and Computation of Reactions and Properties in Solutions and Liquids

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ISHIDA, Tateki
Assistant Professor

We focus on the projects on ionic liquids (ILs). ILs' projects include both the unique dissolution process of cellulose polysaccharides and the investigation of statical and dynamical properties on ionic liquids.

1. Investigations of Dissolution and Decomposition Mechanisms of a Cellulose Fiber in Ionic Liquids[1] with Molecular Dynamics Simulation

We carried out the studies of dissolution and decomposition mechanisms of cellulose (I_β) polymers in ILs. In order to investigate motion of cellulose fibers and intermolecular interactions between cellulose molecules and cationic and anionic species in ILs. We employed the 1-ethyl-3-methylimidazolium acetate IL solvent for target system. From molecular dynamics simulation results, it was found out that the intermolecular interaction energy between cellulose polymers in the IL are reduced, comparing with that in water. Also, our results suggest that the enhancement of the flexibility of rigid cellulose chains triggered by the breakage of intrachain H-bonds due to anions starts decomposition processes accompanied by dissolution processes due to the intercalation of cations, synergistically, and, then, both dissolution and decomposition processes are executed simultaneously.

2. Researches on Statical and Dynamical Properties of Ionic Liquids: Molecular Origin of Low-k Peak of ILs and Dynamical Heterogeneity

We have investigated the molecular level origin of low-k peak (< 0.5 Ang.$^{-1}$) in the structure factor in ILs. In particular, we found out that the structure factor of heterocyclic ring parts in cations largely contribute to low-k peak in ILs. Also, we are going to carry out the study of dynamical properties of ILs, dynamical heterogeneity in ILs at room temperature with molecular dynamics simulation procedure.

Reference

1) T. Ishida, *J. Phys. Chem. B* **124**, 3090–3102 (2020).

Visiting Professors

Visiting Professor

MORI, Hirotoshi *(from Chuo University)*

Electronic Structure Informatics for Designing Functional Liquid Materials

Mixed liquids exhibit various chemical functions depending on their composition and mixing ratio. Contrary to its fundamental scientific importance, however, the chemistry of mixing is an area where molecular level knowledge is not still enough. With the backgrounds, we have been challenging the predictive chemistry of functional liquid materials by developing a novel *ab initio* molecular simulation method with conventional computational cost (Effective fragment potential molecular dynamics; EFP-MD) and a data science approach. In fiscal 2020, we worked on the prediction of Henry's constant values related to the absorption of various industrial exhaust gases for non-aqueous mixed solutions (mixed ionic liquids, ionic liquids/organic solvent mixtures) which supports environmental chemical engineers shortly. We will proceed with our research aiming at the construction of statistical thermodynamic theory for real systems that predict mixed thermodynamics.

Visiting Professor

YANASE, Youichi *(from Kyoto University)*

Theoretical Study of Exotic Quantum Phases

We are working on theoretical studies of exotic quantum phases such as unconventional superconductivity, parity-violating magnet, quantum liquid crystal, and topological states of matter. In particular, our recent interest focuses on quantum phases lacking global or local space inversion symmetry. This year, we studied exotic superconductivity such as odd-parity superconductivity, odd-frequency superconductivity, noncentrosymmetric superconductivity, and ferroelectric superconductivity. Target materials include transition metal dichalcogenides such as MoS_2, heavy fermion superconductors such as UTe_2 and $CeRh_2As_2$, and perovskite oxides such as $SrTiO_3$. Interestingly, most of them are candidates of topological superconductors. We also explored new functionalities of superconductors and magnets. For instance, superconducting diode effect, giant surface Edelstein effect in d-wave superconductors, chiral photocurrent generation in parity-violating antiferromagnet, and nonlinear electric transport have been theoretically clarified, and candidate materials have been proposed.

Visiting Associate Professor

HIGASHI, Masahiro *(from Kyoto University)*

Theoretical Study on the Excited-State Reactions in Condensed Phases

We are theoretically investigating chemical reactions and physical properties in condensed phases such as solutions and proteins. In particular, we are focusing on the excited-state reactions in condensed phases. The excited-state reaction dynamics of large systems are still one of most challenging subjects in theoretical chemistry due to the high computational cost of quantum chemical calculations for excited states and adequate statistical samplings required for molecular dynamics simulations. To overcome these difficulties, we have been developing several efficient methods combining quantum chemical calculations and molecular dynamics simulations. Recently, we analyzed the excitation energy transfer in a light-harvesting complex by using our developed methods and found that the efficient excitation energy transfer is achieved by the site-dependent fluctuations. We are now investigating the primary charge separation in photosynthetic reaction centers and the photoexcited charge separation in organic solar cells. We will reveal molecular mechanisms of environmental effects in both systems.

RESEARCH ACTIVITIES
Photo-Molecular Science

We study the interaction of atoms and molecules with optical fields with its possible applications to active control of atomic and molecular functionality and reactivity. We also develop novel light sources to promote those studies. Two research facilities, the Center for Mesoscopic Sciences and the UVSOR Synchrotron Facility, closely collaborates with the Department.

The core topics of the Department include attosecond coherent control of gas- and condensed-phase atoms and molecules, high-resolution optical microscopy applied to nanomaterials, synchrotron-based spectroscopy of core-excited molecules and solid-state materials, vacuum-UV photochemistry, and the development of novel laser- and synchrotron-radiation sources.

Ultrafast Quantum Simulator and Computer

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2007 Visiting Professor, Tokyo Institute of Technology (–2008)
2009 Visiting Professor, The University of Tokyo (–2011)
2012 Visiting Professor (Humboldt Awardee), University of Heidelberg
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Awards
1998 Award by Research Foundation for Opto-Science and Technology
2007 JSPS Prize
2007 Japan Academy Medal
2008 Norman Hascoe Distinguished Lecturer, University of Connecticut, USA
2009 Fellow of the American Physical Society
2012 Humboldt Research Award
2017 Hiroshi Takuma Memorial Prize of Matsuo Foundation
2018 Commendation for Science and Technology by the Minister of Education, Culture, Sports, Science and Technology of Japan

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VILLELA, Rene
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Keywords Quantum-Classical Boundary, Quantum Simulation, Quantum Computing

It is observed in a double-slit experiment by Tonomura and coworkers that single electrons recorded as dots on a detector screen build up to show an interference pattern, which is delocalized over the screen.[1)] This observation indicates that a delocalized wave function of an isolated electron interacts with the screen, which is composed of many nuclei and electrons interacting with each other, and becomes localized in space. This change, referred to as "collapse" in quantum theory, is often accepted as a discontinuous change, but a basic question arises: When and how the delocalized wave function becomes localized? Our objective is uncovering this mystery by observing the spatiotemporal evolution of a wave function delocalized over many particles interacting with each other. Having this objective in mind, we have developed coherent control with precisions on the picometer spatial and attosecond temporal scales. Now we apply this ultrafast and ultrahigh-precision coherent control to delocalized wave functions of macroscopic many-particle systems such as an array of ultracold rubidium (Rb) Rydberg atoms, as depicted schematically in Figure 1 and named "ultrafast quantum simulator," envisaging the quantum-classical boundary connected smoothly.

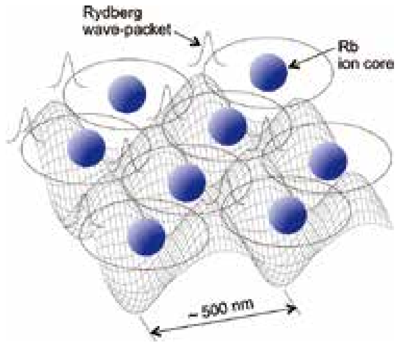

Figure 1. Metal-like quantum gas. A schematic of the many-body quantum simulator with ultracold Rydberg atoms, named "ultrafast quantum simulator," where electronic wave functions spatially overlap between neighboring atoms.[2,7)]

Selected Publications

- H. Katsuki *et al.*, "Visualizing Picometric Quantum Ripples of Ultrafast Wave-Packet Interference," *Science* **311**, 1589–1592 (2006).
- H. Katsuki *et al.*, "Actively Tailored Spatiotemporal Images of Quantum Interference on the Picometer and Femtosecond Scales," *Phys. Rev. Lett.* **102**, 103602 (2009).
- K. Hosaka *et al.*, "Ultrafast Fourier Transform with a Femtosecond-Laser-Driven Molecule," *Phys. Rev. Lett.* **104**, 180501 (2010).
- H. Goto *et al.*, "Strong-Laser-Induced Quantum Interference," *Nat. Phys.* **7**, 383–385 (2011).
- H. Katsuki *et al.*, "All-Optical Control and Visualization of Ultrafast Two-Dimensional Atomic Motions in a Single Crystal of Bismuth," *Nat. Commun.* **4**, 2801 (2013).
- N. Takei *et al.*, "Direct Observation of Ultrafast Many-Body Electron Dynamics in an Ultracold Rydberg Gas," *Nat. Commun.* **7**, 13449 (2016).
- C. Liu *et al.*, "Attosecond Control of Restoration of Electronic Structure Symmetry," *Phys. Rev. Lett.* **121**, 173201 (2018).
- M. Mizoguchi *et al.*, "Ultrafast Creation of Overlapping Rydberg Electrons in an Atomic BEC and Mott-Insulator Lattice," *Phys. Rev. Lett.* **124**, 253201 (2020).

1. Development of an "Ultrafast Quantum Simulator" by Optical Control with Precisions on the Attosecond Temporal and Submicron Spatial Scales[3–10]

Quantum many-body problems are at the heart of a variety of physical functionalities including superconductivity and magnetism in solid materials. It is extremely hard, however, to solve such quantum many-body problems. In solving the Hubbard model with 1000 particles, for example, the diagonalization would take 10 to the power of 573 years even with the world's fastest supercomputers. In this project, we develop a novel quantum simulator that can simulate quantum many-body dynamics for more than 1000 particles within one nanosecond, combining our two unique experimental resources: "coherent control with attosecond precision"[8] and "a strongly-correlated ultracold Rydberg gas."[7,9,10]

We have completed a standard hardware of this ultrafast quantum simulator composed of an array of ultracold Rb atoms trapped in an optical lattice and excited to Rydberg levels with a coherent picosecond (ps) laser pulse, as schematically illustrated in Figure 2.[3,4,6,7,10] The broad bandwidth of the ps laser pulse has allowed us to excite the atoms in the neighboring lattice sites to Rydberg levels simultaneously for the first time. With this standard hardware, we have succeeded in creating an exotic electronic state with spatially overlapping wavefunctions as shown schematically in Figures 1 and 2.[2,4,7,10] The degree of spatial overlap is actively tuned with ~50 nanometer precision. This exotic metal-like quantum gas under exquisite control opens up a completely new regime of many-body physics for simulating ultrafast many-body electron dynamics dominated by Coulomb interactions.[7,10]

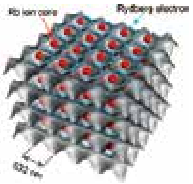

Figure 2. Schematic of the standard hardware of the ultrafast quantum simulator.[3,4,6,7,10]

We have also completed a readout interface of our ultrafast quantum simulator, which is the time domain Ramsey interferometry of ultracold Rydberg atoms with attosecond precision, whose contrast is almost 100% as shown in Figure 3.[5] The phase and visibility of this Ramsey interferogram are highly sensitive to the nature and strength of many-body interactions among the Rydberg atoms.

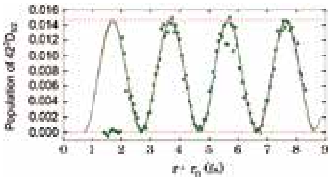

Figure 3. Time domain Ramsey interferometry of ultracold ^{87}Rb atoms with attosecond precision to be used as a readout interface of the ultrafast quantum simulator. Population of the $42^2D_{5/2}$ Rydberg state is plotted as a function of the delay τ between two laser pulses, where τ_0 ~ 50 ps.[5]

2. Application of an "Ultrafast Quantum Simulator" to Quantum Computing[3,10]

We are developing a cold-atom based quantum annealer with the hardware of the ultrafast quantum simulator.[11] The cold-atom quantum annealer has advantages against the one with the superconducting qubits. Those advantages include scalability and efficiency. All to all connections among physical bits necessary for quantum annealing could also be easier with cold atoms than superconducting qubits.

So far we have developed arbitrary two dimensional optical trap arrays for cold atoms, which are necessary for quantum annealing,[11] in tight collaborations with Hamamatsu Photonics K.K.[3,10] Their examples are shown in Figure 4, the world's smallest arbitrary trap arrays whose nearest neighbor distance is only ~1 micron, which used to be typically ~4 micron in previous works.[12]

We have recently succeeded in loading a single atom into each trap of those arbitrary arrays, and reassembling those atoms with an optical tweezer. Accordingly we can prepare an array of atoms we desire, as exemplified in Figure 5.

These techniques mentioned above are also being applied to the development of gate-based quantum computing with cold atoms.

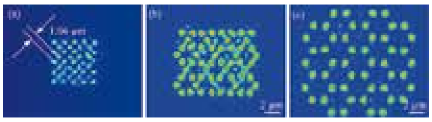

Figure 4. Examples of the world's smallest arbitrary arrays of optical traps. (a) Square lattice; (b) Kagome Lattice; (c) Hexagonal (Honeycomb) lattice.[10]

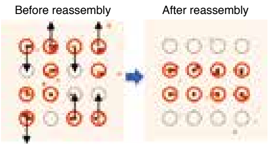

Figure 5. Assembly of an arbitrary array of single Rb atoms.[10]

3. Engineering Quantum Wave-Packet Dispersion with a Strong Nonresonant Femtosecond Laser Pulse[13,14]

A non-dispersing wave packet has been attracting much interest from various scientific and technological viewpoints. However, most quantum systems are accompanied by anharmonicity, so that retardation of quantum wave-packet dispersion is limited to very few examples only under specific conditions and targets. Here we demonstrate a conceptually new and universal method to retard or advance the dispersion of a quantum wave packet through "programmable time shift" induced by a strong nonresonant femtosecond laser pulse. A numerical simulation has verified that a train of such retardation pulses stops wave-packet dispersion.[13,14]

Our ultrafast quantum simulator and computer operates with atomic Rydberg levels,[3–10] whose level structure is anharmonic, so that its wave packet is dispersed and broadened quickly. The new control method for wave-packet dispersion developed here would serve as an enabling technology for our ultrafast quantum simulator and computer to enhance their functionalities.

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Electronic Property of Functional Organic Materials

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	Visiting Professor, Chiba University
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Keywords Photoelectron Spectroscopy, Molecular Assemble, Electronic State

Functional organic materials (FOM) have recently attracted considerable attention both for fundamental research and device applications because of peculiar properties not found in inorganics and small molecules. However, the mechanisms and the origin of various device characteristics are still under debate. Scientific discussions have been redundant because of long-standing beliefs that the electronic structure of FOM would be conserved as in an isolated molecule even for solid phases due to the weak van der Waals interaction. To reveal characteristics of FOM, it is essential to investigate precisely the electronic structure at various interfaces, including organic–organic and organic–inorganic (metal/semiconductor) contacts. Recently we realized that the weak electronic interaction manifests itself as small intensity modulations of fine structures in photoelectron spectra, depending on the adsorption and aggregation conditions on the surface. Thanks to recent instrumentation improvements, we can assess hidden fine features in the electronic states, *e.g.* electron–phonon coupling, quasi-particle states, very small densities of gap states, narrow band dispersion, and dynamic electronic polarization. To elucidate what really impacts on the electronic states of the FOM in their assembly as well as at the interface upon weak interaction, an evaluation of the wave-function spread of the electronic states is very important because the interface states are described as a delocalized molecular orbital state depending on the strength of weak electronic coupling (hybridization). Observing modifications of electron wave functions upon weak electronic coupling as well as strong electron–phonon coupling is a central issue on our agenda.

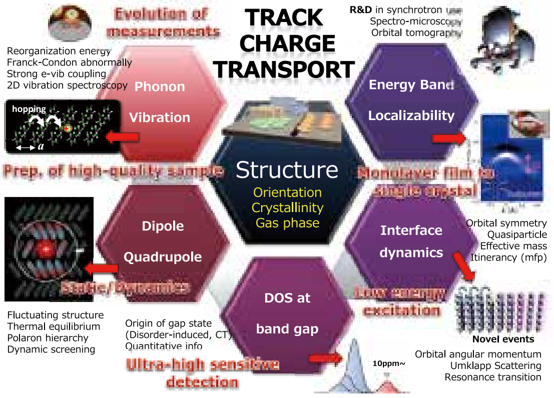

Figure 1. Overview of our agenda. A rich assortment of surface and interface structures of FOM to provide complicated spectral features of ultraviolet photoelectron spectroscopy.

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- Y. Nakayama, S. Kera and N. Ueno, *J. Mater. Chem. C* **8**, 9090–9132 (2020). [review]
- S. Kera, T. Hosokai and S. Duhm, *J. Phys. Soc. Jpn.* **87**, 061008 (7 pages) (2018). [review]
- J.-P. Yang, F. Bussolotti, S. Kera and N. Ueno, *J. Phys. D: Appl. Phys.* **50**, 423002 (45 pages) (2017). [review]
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1. Experimental Observation of Anisotropic of Valence Band Dispersion in the Organic Semiconductor Crystal (DNTT)$^{1)}$

Organic semiconductors based on the aromatic compounds having wide π-conjugation are attracting the attention of researchers because of their applications in various electronic devices. One of the central interests of these materials considering their physicochemical properties is their charge transport mechanism. In general, the conduction of charge carriers in most of the organic semiconductor solids is happening through the intermolecular hopping processes among the discrete molecular orbitals. However, some organic semiconductors with high charge-carrier mobility such as pentacene and rubrene exhibit continuous energy dispersion of valence bands, and the characteristics of the so-called “band transport” have been proposed.

The molecule focused on in this study is dinaphtho[2,3-b:2',3'-*f*]thieno[3,2-*b*]thiophene (DNTT). Although it has been proposed that the transport mechanism of DNTT is a band transport, the valence band dispersion has not yet been observed experimentally. In this study, we elucidate the valence band structure of DNTT single crystals using angle-resolved ultraviolet photoelectron spectroscopy (ARUPS) along three inequivalent crystallographic directions in the surface Brillouin zone. The valence band maximum is verified to be positioned at the Γ point, and the ionization energy of a DNTT single crystal is determined to be 5.02 eV at the VBM. The effective mass of hole is derived from the curvature of the experimental valence band at the Γ point in all three directions, where the lowest value of $2.6m_0$ is measured along the Γ–*S* direction.

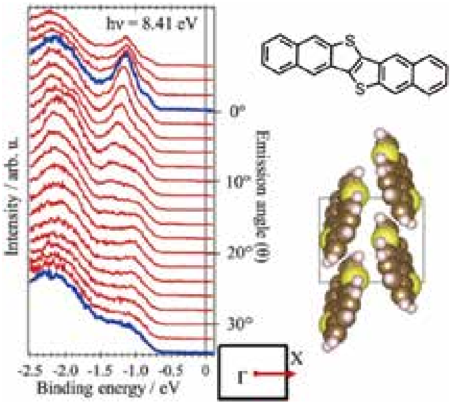

Figure 2. XeI-ARUPS spectra of the DNTT single crystal taken along Γ–*X* direction. The figure is after ref 1).

2. Accessing the Conduction Band Dispersion in $CH_3NH_3PbI_3$ Single Crystal$^{2)}$

The conduction band dispersion in methylammonium lead iodide ($CH_3NH_3PbI_3$), which is a potential candidate for photovoltaic absorbers due to its high-light absorption coefficient, long carrier lifetime and diffusion length, low exciton binding energy, and easy fabrication, was studied both by angle-resolved two photon photoelectron spectroscopy (AR-2PPE) with low photon intensity (~0.0125 nJ/pulse) and angle-resolved low-energy inverse photoelectron spectroscopy (AR-LEIPS). Clear energy dispersions of the conduction band along Γ–*M* direction are observed by these independent methods under different temperatures for the first time, and the dispersion is found to be consistent with band calculation under a cubic phase. The effective mass of the electrons at Γ point is estimated to be $(0.20\pm0.05)m_0$ at 90 K. The observed energy position is significantly different between the AR-LEIPS and AR-2PPE, which is ascribed to the electronic-correlation effects depending on the difference of initial/final state probing processes. The present results also indicate that the surface structure of $CH_3NH_3PbI_3$ is given by a CH_3NH_3 + I plane, which provides the cubic dominated electronic property even at lower temperatures.

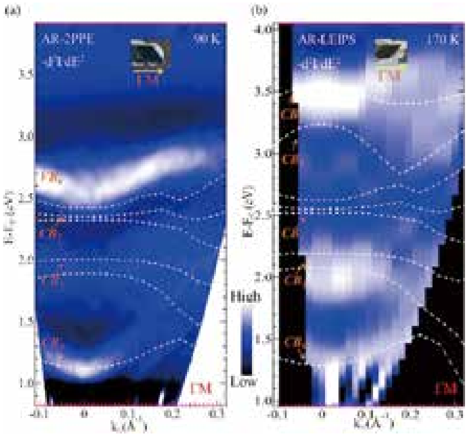

Figure 3. Second-derivative intensity maps of (a) AR-2PPE spectra and (b) AR-LEIPS spectra of $CH_3NH_3PbI_3$ single crystal. The figure is after ref 2).

3. Other Activities in UVSOR

We have conducted beamline R&D and user supports in collaboration with other universities. Experiments using photoelectron momentum microscope are developing at BL6U.$^{3)}$

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Light Source Developments by Using Relativistic Electron Beams

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2004	Professor, Institute for Molecular Science Professor, The Graduate University for Advanced Studies
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Keywords Accelerator, Beam Physics, Synchrotron Radiation

UVSOR is a synchrotron light source providing low energy synchrotron light ranging from terahertz waves to the soft X-rays. Although it was constructed nearly 40 years ago, its performance is still in the world top level particularly among the low energy synchrotron light sources. This is the result of the continuous efforts on improving the machine. Our research group has been developing and introducing new accelerator technologies toward producing brighter synchrotron light with high stability, such as low emittance electron beam optics, novel insertion devices or state-of-the-art beam injection scheme. We have been developing novel light source technologies, such as free electron laser, coherent synchrotron radiation, optical vortices and laser Compton gamma-rays. We have been investigating beam physics which would be the basis of the future developments of the facility.

Figure 1. UVSOR-III Electron Storage Ring and Synchrotron Radiation Beamlines.

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1. Light Source Technology Developments Based on Laser and Synchrotron

We have been developing light source technologies at the UVSOR-III electron storage ring using a dedicated experimental station BL1U, which was constructed under the support of Quantum Beam Technology Program of JST/MEXT aiming to develope novel light sources and exploring their applications. The BL1U is equipped with two undulators which constitute an optical klystron, a laser system which is synchronized with the accelerator beam and a dedicated beamline consisting of mirrors and a monochromator whose arrangement can be flexibly changed according to the types of the experiments.

In these years, we are focusing on generation of spatially structured light, such as optical vortex beams and optical vector beams from undulators, in collaboration with Hiroshima Univ. and Nagoya Univ. We have succeeded in producing such novel photon beams and are exploring their applications. More recently, we have started exploring the possibility utilizing the temporal structure of undulator radiation, in collaboration with Saga Light Source and Toyama Univ. So far, we have been demonstrated the coherent controls of atoms by using radiation from two undulators arranged in tandem. More recently, we have succeeded in observing ultrafast change of an electronic state of an atom, by using tandem undulator radiation.

We have been developing a laser Compton scattering gamma-ray source at BL1U, which is capable of producing monochromatic and energy-tunable gamma-rays. Now we are exploring their applications such as isotope imaging based on nuclear fluorescence resonance in collaboration with Kyoto Univ., AIST and QST, photon-induced positron annihilation lifetime spectroscopy in collaboration with Yamagata Univ. and AIST and an experimental verification on Delbruck scattering in collaboration with QST, AIST and Kyoto Univ. Theoretically we have proven that vortex photons carrying orbital angular momentum can be produced by non-linear Compton scattering of circularly polarized photons. We are planning its experimental demonstration at BL1U in collaboration with AIST.

Figure 2. Twin Polarization-variable Undulators/Optical Klystron at UVSOR-III.

2. Accelerator Technology Developments for Electron Synchrotrons

We carried out several upgrade plans on UVSOR electron synchrotron since 2000. We designed a special beam optics intended to higher brightness. We developed necessary accelerator components, reconstructed the accelerator and commissioned it. We have constructed and commissioned six undulators successfully. Moreover, we have been continuously introducing new accelerator technologies such as the top-up operation in which the electron beam intensity is kept quasi-constant at a high beam current, 300mA, and the novel beam injection scheme with a pulsed sextupole magnet. As the result of all these efforts, now, the machine is one the brightest synchrotron light sources among the low energy machines below 1GeV in the world.

Currently, the storage ring is stably operated for many of the users, however, the requirements from the users for the stability is getting higher and higher. As a near-term upgrade plan, we are considering replacing some of the undulators to fit the changes of the users' requirements on the wavelength. Also, we are seeking a possibility to reduce the emittance with the present magnet configuration. So far, we have found a few beam optics which would give lower emittance around 10 nm. Although they are not compatible with the operation of the narrow gap undulators, they may be used for special experiments which requires lower emittance. For a long-term plan, we continue the design study on a new light source facility. We have been investigating various accelerator systems such as a diffraction-limited synchrotron, an energy recovery linear accelerator and so on. Currently we are focusing on designing a synchrotron with the electron energy of 1 GeV and the circumference of around 70 m. We have designed a synchrotron which would give low emittance of around 6 nm under the achromatic condition.

We are collaborating with Nagoya Univ. and developing new technologies for the future plan. Accelerator magnets based on permanent magnets are being developed, which would contribute to the power consumption saving. New pulsed multipole magnet is also being developed to realize a novel beam injection scheme.

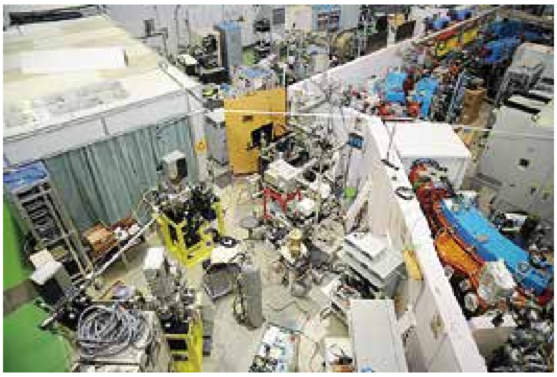

Figure 3. UVSOR BL1U experimental station for source development studies.

Development and Utilization of Novel Quantum Beam Sources Using a High Energy Electron Beam

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2010	Student Presentation Award, The 23rd Annual Meeting of the Japanese Society for Synchrotron Radiation Research
2010	Young Researcher Best Presentation Award, The 53rd Annual Meeting of the Japanese Society of Radiation Chemistry
2011	Nagoya University Outstanding Graduate Student Award
2012	Oral Presentation Award, The 9th Annual Meeting of Particle Accelerator Society of Japan
2012	Young Researcher Best Poster Award, 12th International Symposium on Radiation Physics
2013	Young Scientist Award of the Physical Society of Japan
2015	Young Researcher Best Presentation Award, Beam Physics Workshop 2015

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Keywords Electron Beams, Synchrotron Radiation, Gamma-Rays

Our group develop new electromagnetic wave sources using a high energy electron beam. In the UVSOR-III electron storage ring at the Institute for Molecular Science, a 750-MeV electron beam can be generated. Electromagnetic waves in a wide frequency range from ultraviolet waves to gamma-rays are emitted by interacting the electron beam with magnetic fileds and lasers.

Laser Thomson (Compton) scattering is a method to generate a high energy gamma-ray by the interaction between a high energy electron and a laser. We have developed ultra-short pulsed gamma-rays with the pulse width of sub-ps to ps range by using 90-degree laser Thomson scattering (Figure 1). We applied this ultra-short pulsed gamma-rays to gamma induced positron annihilation lifetime spectroscopy (GiPALS). A positron is an excellent probe of lattice defects in solids and of free volumes in polymers at the sub-nm to nm scale. GiPALS enables defect analysis of a thick material in a few cm because positrons are generated throughout a bulk material via pair production. Our group is conducting research on improving the properties of the material by using GiPALS.

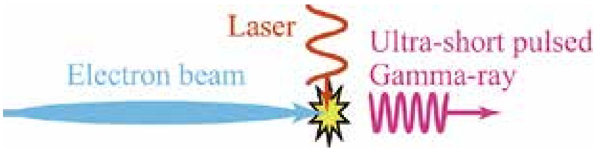

Figure 1. Schematic illustration of 90-degree laser Thomson scattering.

Selected Publications

- Y. Taira, M. Adachi, H. Zen, T. Tanikawa, N. Yamamoto, M. Hosaka, Y. Takashima, K. Soda and M. Katoh, "Generation of Energy-Tunable and Ultra-Short-Pulse Gamma Ray via Inverse Compton Scattering in an Electron Storage Ring," *Nucl. Instrum. Methods Phys. Res., Sect. A* **652**, 696 (2011).
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- Y. Taira and M. Katoh, "Gamma-Ray Vortices Emitted from Nonlinear Inverse Thomson Scattering of a Two-Wavelength Laser Beam," *Phys. Rev. A* **98**, 052130 (2018).
- Y. Taira, M. Fujimoto, S. Ri, M. Hosaka and M. Katoh, "Measurement of the Phase Structure of Elliptically Polarized Undulator Radiation," *New J. Phys.* **22**, 093061 (2020).

1. Gamma-Induced Positron Annihilation Lifetime Spectroscopy (GiPALS)

Positron lifetime spectrum is calculated by measuring the time difference between a reference signal and a detector output for the annihilation gamma-rays, which is emitted when a positron annihilates with an electron inside material. A reference signal is the output of a photodiode located near the injection position of a laser. A BaF_2 scintillator and a photomultiplier tube is utilized to detect the annihilation gamma-rays. Two detectors are arranged at 180 degrees because two annihilation gamma-rays are generated at 180-degree direction. The annihilation gamma-rays are generated to whole solid angle. Therefore array detectors are effective to increase the count rate of the annihilation gamma-rays and to reduce the measurement time. We have developed the array detector using 10 detectors with a help of Equipment Development Center (Figure 2).

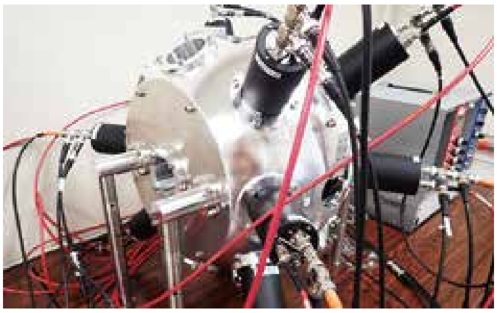

Figure 2. Positron lifetime measurement system using 10 detectors.

Users can currently utilize GiPALS at BL1U in UVSOR-III. A result of defect analysis for a GAGG scintillator was published in 2020.1) We are also developing a new measurement method, gamma ray-induced age-momentum correlation (GiAMOC). On the other hand, we are planning to develop other measurement technique for the annihilation gamma-rays, such as a three-dimensional distribution imaging technique for defects, coincidence Doppler broadening, and spin polarized positrons generated from circularly polarized gamma-rays.

A new laser injection vacuum chamber was installed to the UVSOR-III electron storage ring in April 2021. As both the incoming and outgoing sides of the vacuum chamber are optical windows, the laser can be focused down to 10 micrometers. We have confirmed that the intensity of gamma-rays at the generation point has been improved by a factor of 40.

2. Short Wavelength Optical Vortices

An optical vortex is an electromagnetic wave with a helical phase structure. When an optical vortex beam is viewed in a plane transverse to the direction of propagation, an annular intensity profile is observed due to the phase singularity at the center axis. An important consequence of the optical vortex is that it carries orbital angular momentum (OAM) due to the helical phase structure.

While fundamental and applied research on optical vortices using visible wavelength lasers is widely studied, much less has been done in ultraviolet, X-rays, and gamma-rays energy ranges. We have proposed for the first time a method to generate a gamma-ray vortex using nonlinear inverse Thomson scattering of a high energy electron and an intense circularly polarized laser.2) In our method, the circularly polarized laser is important because the helical phase structure arises from the transverse helical motion of the electron inside the circularly polarized laser field. When peak power of a laser achieves terawatt class, high harmonic gamma-rays are generated. Only gamma-rays more than the first harmonic carry OAM. High harmonic gamma-rays show the annular intensity distribution due to this characteristic.

There are few facilities in the world, where can carry out the experiment for the nonlinear inverse Thomson scattering using an intense circularly polarized laser in terawatt class. We carried out the experiment at Kansai Photon Science Institute in Japan, where a 150 MeV microtron and a petawatt laser are available. Although we were not able to achieve the measurement of an annular intensity distribution of high harmonic gamma-rays, we plan to continue the experiment this year.

On the other hand, optical vortices in the ultraviolet wavelength range can be generated using a helical undulator. Similar with a nonlinear inverse Thomson scattering, an electron obeys a helical trajectory inside an undulator. Therefore, high harmonic radiation emitted from a helical undulator forms the helical phase structure.

Generation of an optical vortex from a helical undulator has been demonstrated at UVSOR-III. Recently, we newly revealed that undulator radiation with the phase structure can be generated from an elliptically polarized undulator.2) We derived the analytic expressions for the emitted electric fields were fully derived and the radiation's phase structure was found to change according to polarization. Average phase gradients of the undulator's radiation were measured using a double slit interferometer. The measured phase gradients of the first through third harmonics were compared with the calculated results.

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Award

TAIRA, Yoshitaka; The Outstanding Presentation Award of the 64th Annual Meeting of the Japanese Society of Radiation Chemistry (2021).

* carrying out graduate research on Cooperative Education Program of IMS with Nagoya University

Angle-Resolved Photoemission Study on Strongly Correlated Electron Materials

UVSOR Synchrotron Facility
Division of Advanced Solid State Physics

Education
2000 B.S. The University of Tokyo
2005 Ph.D. The University of Tokyo

Professional Employment
2005 Postdoctoral Fellow, Stanford University and Lawrence Berkeley National Laboratory
2008 Assistant Professor, Osaka University
2013 Associate Professor, Osaka University
2014 Associate Professor, Institute for Molecular Science
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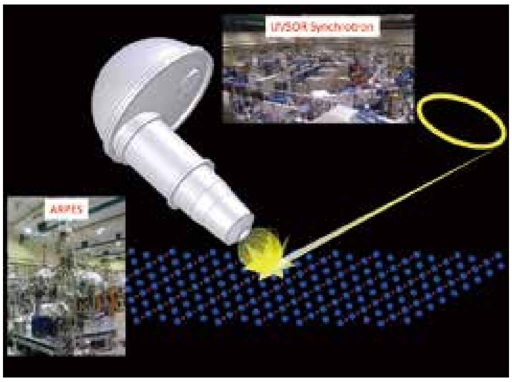
Keywords Strongly Correlated Electron System, Synchrotron Light, Photoemission

Strongly correlated electron materials has attracted more attentions in the last few decades because of their unusual and fascinating properties such as high-T_c superconductivity, giant magnetoresistance, heavy fermion and so on. Those unique properties can offer a route toward the next-generation devices. We investigate the mechanism of the physical properties as well as the electronic structure of those materials by using angle-resolved photoemission spectroscopy (ARPES). ARPES is a powerful experimental technique, directly measuring the energy (E) and momentum (k) relation, namely the band structure of solids. In the last quarter of a century, the energy resolution and angular resolution of ARPES have improved almost three order of magnitude better, which makes us possible to address the fine structure of the electronic structure near the Fermi level: Superconducting gap, kink structure and so on. The main target materials of our group is high-T_c superconductors, such as cuprates and iron pnictides and use UVSOR-III as a strong light source.

Our group is also developing high-efficiency spin-resolved ARPES system. Spintronics is a rapidly emerging field of science and technology that will most likely have a significant impact on the future of all aspects of electronics as we continue to move into the 21st century. Understanding magnetism of surfaces, interfaces, and nanostructures is greatly important for realizing the spintronics which aims to control and use the function of spin as well as the charge of electrons. Spin-resolved ARPES is one of the most powerful experimental techniques to investigate the magnetic properties of such materials.



Selected Publications

- K. Tanaka, W. S. Lee, D. H. Lu, A. Fujimori, T. Fujii, Risdiana, I. Terasaki, D. J. Scalapino, T. P. Devereaux, Z. Hussain and Z.-X. Shen, "Distinct Fermi-Momentum-Dependent Energy Gaps in Deeply Underdoped Bi2212," *Science* **314**, 1910–1913 (2006).
- W. S. Lee, I. M. Vishik, K. Tanaka, D. H. Lu, T. Sasagawa, N. Nagaosa, T. P. Devereaux, Z. Hussain and Z.-X. Shen, "Abrupt Onset of a Second Energy Gap at the Superconducting Transition of Underdoped Bi2212," *Nature* **450**, 81–84 (2007).
- K. Tanaka, N. Hieu, G. Vincini, T. Masui, S. Miyasaka, S. Tajima and T. Sasagawa, "Quantitative Comparison between Electronic Raman Scattering and Angle-Resolved Photoemission Spectra in $Bi_2Sr_2CaCu_2O_{8+\delta}$ Superconductors: Doping Dependence of Nodal and Antinodal Superconducting Gaps," *J. Phys. Soc. Jpn.* **88**, 044710 (2019).
- S. Ideta, N. Murai, M. Nakajima, R. Kajimto and K. Tanaka, "Experimental Investigation of the Suppressed Superconducting Gap and Double-Resonance Mode in $Ba_{1-x}K_xFe_2As_2$," *Phys. Rev. B* **100**, 235135 (7 pages) (2019).

1. Development of Spin-Resolved ARPES with Image-Spin Detection

Spintronics is a rapidly emerging field of science and technology that will most likely have a significant impact on the future of all aspects of electronics as we continue to move into the 21st century. Understanding magnetism of surfaces, interfaces, and nanostructures is greatly important for realizing the spintronics which aims to control and use the function of spin as well as the charge of electrons. Spin- and angle-resolved photoemission spectroscopy (spin-resolved ARPES) is one of the most powerful experimental techniques to investigate the magnetic properties of such materials, where one can know the “complete” information of the electronic states of materials; energy, momentum, and spin direction. Recent development of high energy and angle resolved photoelectron analyzer as well as the contemporary light sources such as third generation synchrotron radiation make it possible for the photoemission spectroscopy to investigate not only band structures but many body interactions of electrons in solids. However, appending the spin resolution to photoemission spectroscopy is quite difficult because of an extremely low efficiency (10^{-4}) of Mott-type spin detections. Recently, very-low-energy-electron-diffraction (VLEED-type) spin detector with 100 times higher efficiency than that of conventional Mott-type has been developed and spin-resolved ARPES has been started to be realized. So far, most of the spin-resolved ARPES systems in the world are using the single-channel detector and efficiency is still a problem.

Beamline BL5U at UVSOR has been totally reconstructed by our group, and opened for users as high photon flux and high energy resolution ARPES beamline since 2017. As a new function for this beamline, we have started high-efficient spin-resolved ARPES project with multi-channel detection (we call “image-spin” detection). The goal of this project is to realize the 100 times better efficiency and the 10 times better momentum resolution than the current spin-resolved ARPES system in the world, which can be a breakthrough in this field.

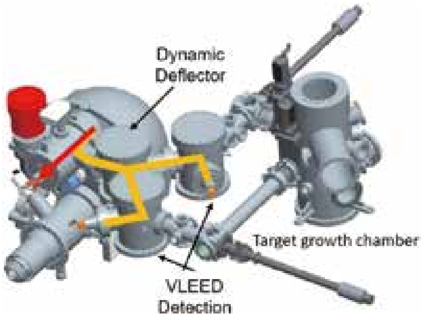


Figure 1. Current setup of image-spin ARPES.

In 2020, we set up the spin detection system and finished the adjustment of the electron lens parameters of the spin detection part (Figure 1). Finally, we successfully obtained spin-resolved signal of Au(111) surface as shown in Figure 2. According to the rough estimation, the efficiency is 100 times better and the momentum resolution is several times better than the current spin-resolved ARPES system in the world.

2. Strong Relationship between ARPES Superconducting Spectral Weight and T_c [1,2]

Our resent ARPES study on high-T_c cuprate superconductors $Bi_2Sr_2CaCu_2O_{6+\delta}$ (Bi2212) and $Bi_2Sr_2Ca_2Cu_3O_{10+\delta}$ (Bi2223) indicated strong relationship between the superconducting spectral weight and the critical temperature T_c. To see the detail, we are performing temperature and carrier concentration dependent measurements on several kinds of high-T_c cuprate superconductors.

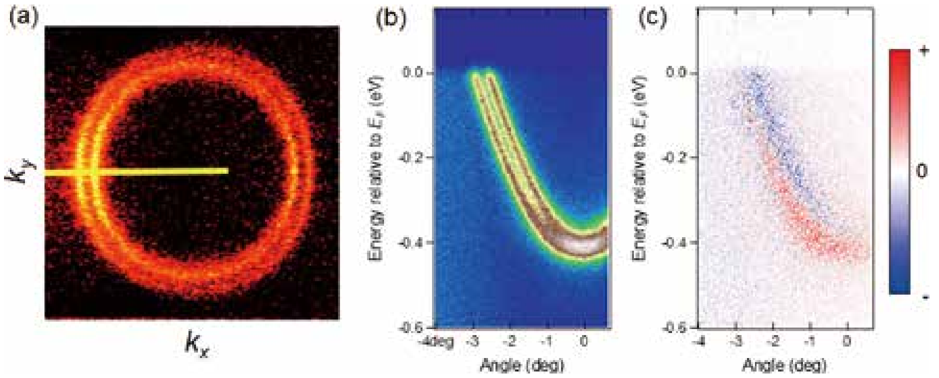


Figure 2. (a) Fermi surface of Rashba spin splitting in Au(111) surface states and (b) image plot of normal ARPES at yellow bar in (a). (c) Spin-resolved ARPES showing the spin polarization (blue–red scale).

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* Present Address; Hiroshima University

† carrying out graduate research on Cooperative Education Program of IMS with Nagoya University

Photoemission Imaging in *k* and *r* Spaces

UVSOR Synchrotron Facility
Division of Beam Physics and Diagnostics Research

MATSUI, Fumihiko
Senior Researcher

Complete measurements of photoelectron, including three- dimensional spin degrees of freedom are challenging techniques for pioneering electron spin physics and spintronics. We are developing a new system that combines a photoelectron momentum microscope (PMM), two-dimensional spin filter, and a synchrotron light source. Our goal is to achieve reliable electronic structure analysis by complete photoelectron measurement of band dispersion and core levels, and link it to developments and applications of materials and devices.

1. Photoelectron Momentum Microscope

We have built a new PMM station for 3D momentum-resolved photoelectron spectroscopy with a microscopic field of view at the soft X-ray beamline BL6U of UVSOR. The details of the specification evaluation result are described elsewhere.1) In brief, the energy, spatial, and momentum resolutions of the analyzer were estimated to be 20 meV, 50 nm, and 0.012 Å^{-1}, respectively. Samples can be cooled down to 8 K and heated up to 400 K.

A gold checkerboard pattern on a Si wafer imaged by a microscopy mode is shown in Figure 1. Elemental specific information is obtained by spectro-microscopy as shown in Figure 1(b) and (c). Figure 2 shows an example of 3D valence band dispersion imaging by a momentum mode.

With a photon energy range up to 800 eV covered by the BL6U, core-level excitation of a variety of important elements including C, N, O and transition metals is possible. Specific atomic sites and electronic states can be selectively characterized by the resonant Auger process. Resonant momentum-resolved photoelectron spectroscopy is a method unique to this station that opens the door to elemental- and orbital-selective valence band dispersion analysis.

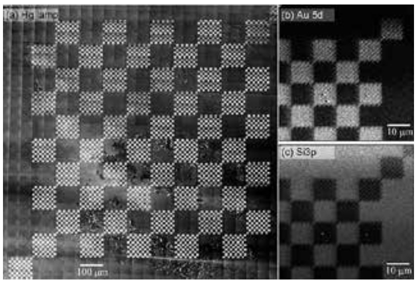

Figure 1. Real-space valence photoelectron images of a gold checkerboard pattern observed using (a) Hg lamp and (b)–(c) synchrotron radiation ($hv = 60$ eV) as excitation.2)

Figure 2. (a) Stereograph of valence band dispersion of graphite crystal surface. A parabolic π band with six Dirac points is imaged.

2. Original Analyzers towards Spin Imaging

Furthermore, we are aiming at highly efficient and comprehensive measurement of spin distribution as the final goal. *Omnidirectional photoelectron acceptance lens* (OPAL)3) together with *Projection-type electron spectroscopy collimator analyzer* (PESCATORA)4) enables photoelectron holography measurement of the full hemisphere. Moreover, we invented *Right angle deflection imaging analyzer* (RADIAN)5) for spin vector analysis with ***k***/***r***-space resolution. We are expanding the MM system based on our original inventions.

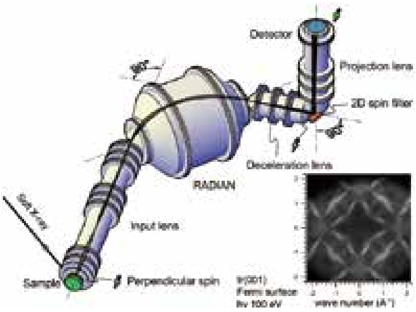

Figure 3. Schematic diagram of 3D-spin distribution projection analysis system.5) Inset is the Fermi surface of the Ir(001) thin film for a 2D spin filter target measured by UVSOR-PMM.

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Award

MATSUI, Fumihiko; NAGAI Foundation for Science & Technology Encouragement Award (2021).

Soft X-Ray Absorption Spectroscopy for Observing Chemical Processes in Solution

Department of Photo-Molecular Science
Division of Photo-Molecular Science III

NAGASAKA, Masanari
Assistant Professor

Soft X-ray absorption spectroscopy (XAS) observes local structures of liquids with different light elements. We have developed liquid cells and devices with precise absorbance control and observed several chemical processes in solution by using *operando* XAS.[1] In this year, we have developed an ultrathin liquid cell for XAS of liquids in the low-energy region below 200 eV.

1. Development of the Ultrathin Liquid Cell for XAS in the Low-Energy Region

XAS below 200 eV is important for chemical research since it includes K-edges of Li and B and L-edges of Si, P, S, and Cl. Recently, we have established soft X-ray transmission argon gas window that is effective from 60 to 240 eV.[2] From soft X-ray transmission calculations, soft X-rays below 200 eV can transmit argon gas with the optical length of 2.6 mm. As shown in Figure 1, we have developed the ultrathin liquid cell that realize the 2.6 mm optical length of argon gas. XAS spectra of 2 M LiCl aqueous solution at Li K-edge and Cl L-edge were successfully obtained by using this liquid cell.

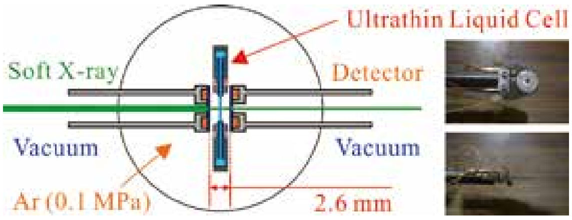

Figure 1. The schematic and photographs of the ultrathin liquid cell for XAS measurements of liquids in the low-energy region.

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Distribution of Biological Molecules in a Cell Nucleus Analyzed by 3-Dimensional Spectro-Microscopy

UVSOR Synchrotron Facility
Division of Beam Physics and Diagnostics Research

OHIGASHI, Takuji
Assistant Professor

Scanning transmission X-ray microscopy (STXM) is a promising tool to analyze 2-dimensional chemical state of a sample with high spatial resolution around 30 nm. We have been developing computer tomography (CT) for STXM to perform 3-dimensional spectro-microscopy.[1,2] An isolated cell nucleus of a HeLa S3 cell was used as a sample. 50 datasets of 2-dimensional X-ray absorption spectra (2D XAS) of the sample around O K-edge was acquired with rotating the sample 3.6° each (180° rotation in total). 3D XAS of the cell nucleus is reconstructed from 50 datasets of 2D XAS. Distributions of DNA (red) and protein (green) are obtained by fitting reference spectra to the 3D XAS by single value decomposition algorithm (Figure 1). In cross sectional images, nucleoli and network structure of protein around them can be distinguished clearly. A goal of this research is to elucidate chemical and morphological change of biological molecules through a process of apoptosis.

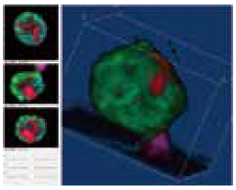

Figure 1. 3-dimensional distributions of DNA (red) and protein (green) in a HeLa S3 cell nucleus. Left panels are cross sectional images and a right panel is volume rendering image.

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Mesoscopic Structures of Liquid-Crystal Molecules Probed by Resonant Soft X-Ray Scattering

UVSOR Synchrotron Facility
Division of Advanced Photochemistry

IWAYAMA, Hiroshi
Assistant Professor

We study soft matters such as liquid-crystal materials with soft x-ray, whose energy region covers K-edge energies of carbon, nitrogen and oxygen. Soft matters exhibit their intriguing properties due to mesoscopic physical structures by self-organizations. To understand properties of soft matters, we need to investigate their structure in the mesoscopic scale.

1. Resonant Soft X-Ray Scattering Method

Resonant soft x-ray scattering measurements can probe mesoscopic structures and periodic spatial variations of the orientation of molecules with both elemental and chemical environment sensitivity and have orders of magnitude scattering intensity enhancement over conventional small angle (non-resonant) x-ray scattering, which is sensitive only to the electron density modulations.

In this year, we performed RSoXS experiments at UVSOR BL3U for the first time. Our sample is S-MHPOBC, which is a chiral smectic liquid crystal molecule and shows ferro- and antiferroelectric phases depending on its temperature.

We successfully obtained diffraction images at the wavelength of 4.34 nm (285 eV), which correspond to C 1s-to-π^* core excitations. From the analysis of images, we found a resonant enhancement of diffractions corresponding to a period length of 6.4 nm. Considering single molecular length of 3 nm, this shows the sample is antiferroelectric under the measurement conditions. We investigate intermediate phases between ferro- and antiferroelectric one by changing sample temperatures.

Visiting Professors

Visiting Professor

FUKUI, Ken-ichi *(from Osaka University)*

Ionic Liquid/Organic Semiconductor Film Interfaces for Efficient Carrier Transport

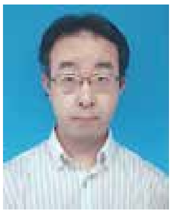
Local analyses of electrolyte/organic semiconductor electrode interfaces at controlled electrode potentials are of fundamental importance to understanding the origin and properties of the electric double layer (EDL) at the interfaces, which is necessary for their application to EDL-organic field effect transistors (OFETs). Ionic liquids (ILs) gated EDL-OFETs can be operated with ultralow threshold voltage (~0.1 V), and high electric field of the EDL restrict the hole carrier at the organic molecular facing the interface, thus a few molecular layer film works as the efficient device. By adopting newly developed electrochemical ATR-FUV (EC-ATR-FUV) system for the analyses of electronic states of the device consisting of a two-layer-thick C9-DNBDT-NW film and an IL (EMIM-FSA), we have succeeded to obtaining the hole carrier density as low as 1/500 hole per a C9-DNBDT-NW molecule. The spectrum analyses also provided the information of interaction between the organic thin film and the IL. Further analyses of the system using UVSOR are in progress.

Visiting Professor

SHIMADA, Kenya *(from Hiroshima University)*

High-Resolution Angle-Resolved Photoemission Study of Topological Materials

By means of high-resolution angle-resolved photoemission spectroscopy (ARPES), we clarify electronic structures of solids (band structures, Fermi surface, spin polarization) to understand their physical properties from the microscopic point of view. This year, we have examined the antiferromagnetic topological insulator families $(Bi_2Te_3)_nMnBi_2Te_4$ (n = 1,2). We have observed the electronic band structures specific to the surface termination, which are fully consistent with detailed density functional theory (DFT) calculations. It indicates the surface termination is important for the surface states on $(Bi_2Te_3)_nMnBi_2Te_4$. We have also examined the spin texture of a photocatalyst BiOI. There are two Bi-I sectors connected via the centrosymmetric point, and we found that the topmost iodine layer had a helical spin texture with a spin polarization up to ~80%. Based on the detailed theoretical considerations, the high spin polarization on each sector is protected by the non-symmorphic lattice symmetry (P4/nmm) together with the strong spin–orbit interaction. We have confirmed that the spin-momentum-layer locking effect in BiOI. To improve the spatial resolution of high-resolution ARPES on the HiSOR beamline, we have introduced a highly precise XYZ translator with the absolute accuracy of <1µm and developed the spatial mapping mode.



Visiting Associate Professor

KATSUKI, Hiroyuki *(from Nara Institute of Science and Technology)*

Coherent Control in Condensed Systems

Coherent control is a technique to manipulate quantum states of a target system utilizing the interference of wavefunctions. Highly designed ultrashort laser pulses, both temporally- and spatially-modulated, are used to manipulate the amplitudes and phases of the target wavefunctions. Current my research is focused on the coherent control in various condensed phase systems including strongly coupled systems composed of cavity photons and molecular excited states. Especially, vibrational polaritons which are composed of the molecular vibrational states and mid-infrared cavity photons are of great interest due to the possibility to manipulate the dynamics of chemical reactions. This is possible since the ground state potential surface is locally modulated by the formation of polaritons. Now we are preparing a femtosecond pump–probe and other nonlinear spectroscopic setups to track the ultrafast dynamics of such strongly coupled vibrational polariton systems.

RESEARCH ACTIVITIES

Materials Molecular Science

Extensive developments of new functional molecules and their assemblies are being conducted in three Divisions of Electronic Structures, Electronic Properties, and Molecular Functions, and one division for visiting professors and associate professors, in an attempt to discover new phenomena and useful functions. The physical (electric, optical, thermal and magnetic) properties on new functional materials, the chemical properties like enzymes, catalysis and photochemistry, the exploitation of new spectroscopic methods for materials molecular science, and technological applications like batteries, photocatalysts, fuel cells, solar cells and field effect transistors are investigated in this department.

Exploitation of Novel Spectroscopic Methods for Material and Surface Science

Department of Materials Molecular Science
Division of Electronic Structure

YOKOYAMA, Toshihiko
Professor
[yokoyama@ims.ac.jp]

Education

1983	B.S. The University of Tokyo
1985	M.S. The University of Tokyo
1990	Ph.D. The University of Tokyo

Professional Employment

1987	Research Associate, Hiroshima University
1993	Research Associate, The University of Tokyo
1994	Lecturer, The University of Tokyo
1996	Associate Professor, The University of Tokyo
2002	Professor, Institute for Molecular Science Professor, The Graduate University for Advanced Studies

Member
Assistant Professor
KOITAYA, Takanori
YAMAMOTO, Kohei
Secretary
ISHIKAWA, Azusa

Keywords X-Ray Absorption Spectroscopy, Surface & Thin Film Magnetism, Ambient Pressure Hard and Soft X-Ray Photoelectron Spectroscopy

For the developments of novel functional materials, it is quite important to exploit simultaneously new analytical methods based on advanced technology. Novel materials and devices often require spatial and/or time resolved analysis to optimize their qualities. In our group, we have been exploiting spectroscopic methods for material and surface science using mainly synchrotron radiation (SR) and partly lasers.

The first subject in our group is the spectroscopic analysis systems of magnetic thin films. In 2006, we successfully invented a novel magnetic nanoscope using ultraviolet magnetic circular dichroism (UV MCD) photoelectron emission microscopy (PEEM), which allows us to perform real-time and ultrafast magnetic imaging to investigate magnetic dynamics. We have also constructed in situ x-ray magnetic circular dichroism (XMCD) system using an ultrahigh vacuum superconducting magnet and a liq. He cryostat, which is installed at Beamline 4B of the IMS SR facility UVSOR-III. The apparatus is extensively open for public usage. Recently, assistant professor Kohei Yamamoto is developing the soft x-ray resonant magnetic reflectivity (SXRMR) system for the clarification of depth resolved magnetism of magnetic thin films with the atomic layer resolution scale, and is conducting coherent diffraction imaging (CDI) experiments for the observation of magnetic domain structures of magnetic thin films, using highly coherent SR x-rays from SPring-8 hard x-ray undulators and x-ray free electron laser SACLA. By combining the SXRMR and CDI experiments, the magnetic structures along both the vertical and lateral directions can be revealed with atomic to nm spatial resolution.

The second subject is the exploitation of ambient pressure hard x-ray photoelectron spectroscopy (AP-HAXPES) for polymer electrolyte fuel cells (PEFC) under working conditions. Although photoelectron spectroscopic measurement is usually done under ultrahigh vacuum, recent material science requires ambient pressure measurements under working conditions. In 2017, we succeeded in real ambient pressure (10^5 Pa) HAXPES measurements for the first time using Beamline 36XU of SPring-8. Moreover, we designed and constructed the subsecond time resolved AP-HAXPES measurement system, and successfully investigated electrochemical reaction dynamics for the cathode Pt oxidation/reduction and the S^2-adsorption/desorption processes upon an abrupt step of the cathode-anode bias voltages. These works were supported by the NEDO Fuel Cell project. More recently, assistant professor, Takanori Koitaya, has been investigating various kinds of surface chemical reactions such as methane activation and CO_2 hydrogenation using the AP-HAXPES system combined with the near ambient pressure soft x-ray photoelectron spectroscopy system installed at Beamline 07LSU of SPring-8.

Selected Publications

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- T. Yokoyama and K. Eguchi, *Phys. Rev. Lett.* **107**, 065901 (2011).
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- Y. Takagi *et al.*, *Appl. Phys. Express* **10**, 076603 (2017).
- Y. Uemura *et al.*, *Chem. Commun.* **53**, 7314 (2017).
- Y. Takagi *et al.*, *Acc. Chem. Res.* **51**, 719 (2018).
- L. Yu *et al.*, *J. Phys. Chem. C* **123**, 603 (2019).
- T. Nakamura *et al.*, *J. Phys. Chem. C* **124**, 17520 (2020).
- S. Chaveanghong *et al.*, *Phys. Chem. Chem. Phys.* **23**, 3866 (2021).

1. Sulfur Poisoning Pt and PtCo Anode and Cathode Catalysts in PEFC Studied by *operando* AP-HAXPES[1)]

In practical performance of polymer electrolyte fuel cells (PEFC), the Pt_3Co alloy electrode is known to be superior to the pure Pt electrode because of a longer life time and a less amount of noble Pt metal. In this work, in order to evaluate the tolerance of S poisoning between Pt_3Co and Pt electrodes comparatively, we have investigated the S adsorption behaviours on Pt (average particle size ~2.6 nm) and Pt_3Co (~3.0 nm) anode and cathode electrode catalysts in PEFC under working conditions for the fresh state just after the aging process and also the degraded state after accelerated degradation tests (ADT), by recording near ambient pressure HAXPES.

The S 1s HAXPES of both the anode and cathode electrodes show not only the principal S species from the sulfonic acid group ($-SO_3H$) in the Nafion electrolyte (~2478 eV in the left panel of Figure 1) but also other characteristic S species such as zero-valent S (S^0) adsorbed on the carbon support (~2471 eV) and anionic S (S^{2-}) adsorbed on the Pt electrode (~2470 eV). The S^{2-} species on Pt should be ascribed to S contamination poisoning the Pt catalyst electrode. The S^{2-} species on the cathode can be oxidatively removed by applying a high cathode–anode bias voltage (≥ 0.8 V) to form SO_3^{2-}, while at the anode the S^{2-} species cannot be eliminated because of reductive environment in hydrogen gases. The important finding is the different S adsorption behaviour between the Pt/C and Pt_3Co/C electrodes after ADT. After ADT, the Pt/C anode electrode exhibits much larger S^{2-} adsorption than the Pt_3Co/C anode electrode. This indicates that the Pt_3Co/C anode is more desirable than the Pt/C one from the view point of S poisoning.

The reason for more tolerance of the Pt_3Co/C anode catalyst against S poisoning after ADT can be ascribed to more negative charge of the surface Pt atoms in the Pt_3Co/C catalyst than the Pt/C one, this yielding weaker interaction between the surface Pt and the anionic S species as S^{2-}, SO_3^{2-}, and SO_4^{2-}. A similar behaviour was observed also in the cathode catalyst. The present findings will nevertheless provide important information to design novel Pt-based PEFC electrodes with higher performance and longer durability.

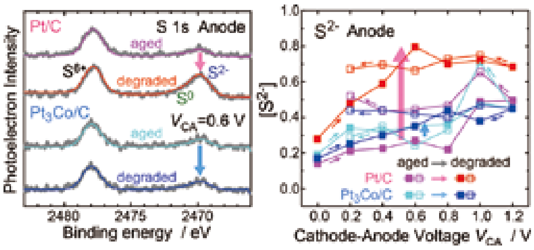

Figure 1. (left) Typical S 1s HAXPES from the anode Pt/C and Pt_3Co/C electrodes at the cathode–anode voltage V_{CA} = 0.6 V for the aged (before ADT) and degraded (after ADT) PEFC. The S^{2-} peak intensity (~2470 eV) is found to increase significantly in Pt/C, while it is not so much in Pt_3Co/C. (right) The relative amount of S^{2-} with respect to S^{6+} originating from Nafion $-SO_3H$, for the aged and degraded anode Pt/C and Pt_3Co/C electrodes, as a function of V_{CA}. It is clearly exemplified that the Pt_3Co/C anode electrode is more tolerant against S poisoning than the Pt/C.

2. Negative Thermal Expansion of Zinc-Blende CdTe from the View Point of Local Structure

Since the discovery of anomalously large negative thermal expansion (NTE) in ZrW_2O_8 over an extremely wide temperature range in 1996, NTE has revived as a hot topic in structural solid-state chemistry and physics. The origin of zero thermal expansion and/or NTE is known to be categorized into two mechanisms. The first one is a so-called Invar effect as observed in the $Fe_{64}Ni_{36}$ Invar alloy, in which the electronic structure of some atoms in the system is temperature dependent. The second one is derived from vibrational anomaly. The materials with zinc blende or diamond structure mostly show NTE at low temperature due to the presence of vibrational anomaly. In this work, thermal expansion of zinc-blende CdTe was investigated from the view point of local structure using the extended x-ray absorption fine structure (EXAFS) spectroscopic data and the path-integral effective classical potential (PIECP) Monte Carlo computational simulations. Figure 2 shows the experimental (EXAFS as orange open circles and XRD as light-blue filled circles) and theoretical (PIECP as solid lines and classical MC as dashed lines). Although the origin of NTE is known as a result of classical vibrational anomaly within the Newton dynamics theory, the quantum statistical simulation is found to be essential to reproduce the negative thermal expansion of CdTe. It is emphasized that the vibrational quantum effect and classical anharmonicity are of great importance for the understanding of low-temperature thermal expansion as well as the elastic constants.

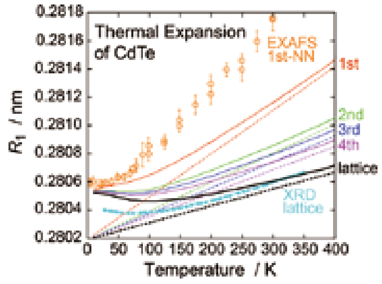

Figure 2. Experimental and theoretical thermal expansion of CdTe. Experimental XRD result for the lattice constant (light-blue closed circles) gives small NTE at <100 K, while experimental EXAFS result for the 1st nearest neighbor shell (orange open circles with error bars) provides quite normal thermal expansion even at low temperature. Computational PIECP results (solid lines) agree qualitatively well with both the experimental EXAFS and XRD data, while the classical MC results failed in the reproduction of the NTE (see black dashed lines).

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1) S. Chaveanghong *et al.*, *Phys. Chem. Chem. Phys.* **23**, 3866–3873 (2021).

Award

KOITAYA, Takanori; 2021 Vacuum and Surface Science Journal Award of the Japan Society of Vacuum and Surface Science (2021).

Exiotic Structures, Physicochemical Properties and Quantum Dynamics of Interfacial Water

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2016 JST-PRESTO Researcher [Innovative Catalysts] (–2019)
2018 Associate Professor, Institute for Molecular Science
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Awards
2014 Young Scientist Award, 33rd Annual Meeting of the SSSJ
2014 39th Vacuum Science Paper Award
2018 PCCP Prize 2018
2018 CSJ Presentation Award 2018
2018 Encouragement Award, The Spectroscopic Society of Japan
2018 Morino Foundation for Molecular Science
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Keywords Surface & Interface Science, Nonlinear Optical Spectroscopy, Water Molecules

Interfacial water is ubiquitous in nature and plays crucial roles in a variety of disciplines, including physics, chemistry and biology. In such a symmetry-breaking system, not only adsorption geometry but also anisotropic molecular orientation (H-up/H-down configuration) is a key structural parameter that determines unique physicochemical properties of interfacial water systems. Nevertheless, orientation of water molecules, *i.e.* configuration of hydrogens, in the interfacial hydrogen-bond network is extremely hard to investigate with traditional experimental techniques such as electron diffraction, grazing X-ray scattering and even scanning prove microscopy, because hydrogen has only a single electron and responds extremely weakly to the probes of these techniques. Therefore, the determination of molecular orientation of interfacial water has been an experimental challenge.

We have used recently developed heterodyne-detected sum-frequency generation spectroscopy for unveiling molecular orientation of interfacial water system. The remarkable feature of this technique is that Im$\chi^{(2)}$ SFG spectra ($\chi^{(2)}$: The second-order nonlinear susceptibility) obtained by the heterodyne detection exhibit positive or negative sign for net orientation of OH with hydrogen pointing away (H-up) or toward substrate (H-down), respectively. Thus, the heterodyne-detected Im$\chi^{(2)}$ SFG has a great advantage to direct observation of water orientation that cannot be investigated through other traditional experimental methods. With this sophisticated molecular spectroscopy technique, we have conducted a series of pioneering research on unique structures and physicochemical properties of hydrogen bonds of interfacial water molecules.

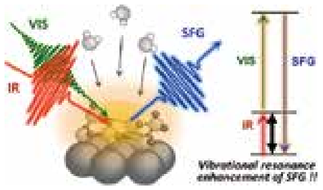

Figure 1. Infrared-visible sum-frequency-generation (SFG) spectroscopy of water molecules on solid surface.

Selected Publications

- T. Sugimoto *et al.*, “Emergent High-T_c Ferroelectric Ordering of Strongly Correlated and Frustrated Protons in Heteroepitaxial Ice Film,” *Nat. Phys.* **12**, 1063–1068 (2016).
- O. Yuji *et al.*, “Unveiling Subsurface Hydrogen-Bond Structure of Hexagonal Water Ice,” *Phys. Rev. B* **96**, 115405 (14 pages) (2017).
- K. Shirai *et al.*, “Water-Assisted Hole Trapping at Highly Curved Surface of Nano-TiO_2 Photocatalyst,” *J. Am. Chem. Soc.* **140**, 1415–1422 (2018).
- T. Sugimoto *et al.*, “Topologically Disordered Mesophase at Topmost Surface of Crystalline Ice Between 120 and 200 K,” *Phys. Rev. B* **99**, 121402(R) (2019).
- F. Kato *et al.*, “Direct Experimental Evidence for Markedly Enhanced Surface Proton Activity Inherent to Water Ice,” *J. Phys. Chem. Lett.* **11**, 2524–2529 (2020).
- T. Sugimoto *et al.*, “Orientational Ordering in Heteroepitaxial Water Ice on Metal Surfaces,” *Phys. Chem. Chem. Phys.* **29**, 16435–17012 (2020).

1. Interface Engineering of the Thermodynamic Properties of Strongly Correlated Many-Body Protons in Crystalline Ice1)

The static and dynamic behavior of strongly correlated protons play crucial roles in rendering exotic properties and enabling a wide range of applications of nanoscale hydrogen-bonded (HB) materials in physics, chemistry and biology. However, because of the difficulty in probing and manipulating the proton configuration in nanomaterials, controlling the cooperative behavior of many-body protons has not been realized.

In this study, we demonstrate the possibility of designing and controlling the physical properties of strongly correlated many-body protons through systematic sum-frequency generation (SFG) spectroscopy of crystalline-ice nanofilms. Since the second-order nonlinear susceptibility tensor $\chi^{(2)}$ is nonzero for non-centrosymmetric systems, the homodyne-detected SFG intensity $|\chi^{(2)}|^2$ increases with increasing the number of water molecules with net orientational preference, and thus can be used as the signature of the emergence of ferroelectric proton ordering. Because of the strong correlation of many-body protons imposed by the ice rules,2,3) protons in the hydrogen-bond (HB) network of crystalline ice provide an interesting platform for studying fundamental emergent properties of strongly correlated proton systems. Here, we employ SFG spectroscopy of heteroepitaxial crystalline-ice nanofilms grown on Pt(111) surface precovered by a well-defined single layer of either carbon monoxide (CO) molecules or oxygen (O) atoms to study the effects of interface termination on mesoscopic characteristics of many-body protons.

The intensities of the $|\chi^{(2)}|^2$-SFG spectra were shown as a function of ice thickness for these substrates (Figure 1). We found that the SFG signal derived from ice film on CO precovered Pt(111) continues to increase as that on bare Pt(111).2,3) In contrast, negligibly small $|\chi^{(2)}|^2$-SFG intensity (Figure1) suggests that ice film on oxygen precovered Pt substrate is paraelectric. Our observations on the two different types of intercalated layer directly demonstrate that the thermodynamic properties of emergent ferroelectric proton ordering are extensively tuned by the interface engineering at the angstrom scale.

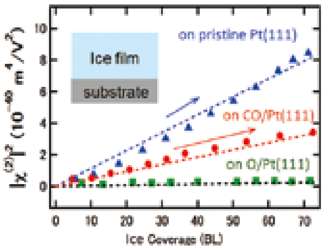

Figure 2. Thickness dependence of the $|\chi^{(2)}|^2$-SFG intensity of crystalline ice films on pristine Pt(111), CO- and O-precovered Pt(111) at 140 K.1)

2. Operando FT-IR Spectroscopy of Steam-Methane-Reforming Photocatalyst under Irradiation of Intensity Modulated UV Light4)

Photocatalytic steam-methane reforming is an attractive chemical technology for hydrogen production from abundant resources of methane and water. In the case of photocatalytic reaction, photo-generated electron plays key roles in hydrogen production. However, the dynamics of photogenerated electrons under reaction condition have been unclear. To uncover the behavior of reactive photo-excited electrons, we conducted *operando* FT-IR spectroscopy of metal loaded Ga_2O_3 photocatalysts under irradiation of intensity modulated UV light. We succeeded in observing a correlation between the reaction activity and a broad mid-infrared absorption band derived from the photo-generated electrons shallowly trapped at the photocatalyst surfaces.

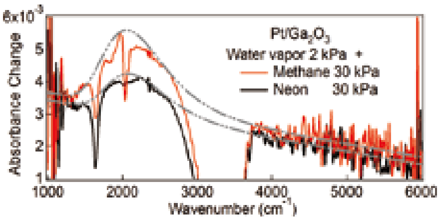

Figure 3. Comparison of the IR absorbance spectra measured in the non-reactive Ne gas and the reactive methane gas environment for Pt loaded Ga_2O_3 photocatalysts.4)

3. Critical Role of Interfacial Water Molcules on the Photocatalytic Methane Activation5)

Recent expectations for effective use of natural gas have led to an interest in chemical technology for methane activation. Photocatalytic approach has a potential to convert methane at ambient conditions. However, the microscopic understanding on photocatalytic reaction mechanism, especially robust C–H bond activation mechanism, remains an open question. Here, combining *in-situ* MS-IR spectroscopy and systematic reaction measurements under various partial pressures of methane and water, we demonstrate that photo-activated interfacial water molecules facilitate the first C–H dissociation and shift the rate-determining step. Our reaction observation on typical three photocatalysts (Ga_2O_3, $NaTaO_3$, TiO_2) clarified the existence of critical partial pressure of methane at approximately 0.5 atm, around which the reaction rates markedly increased with methane partial pressure. *Operand* IR measurements showed that H atom extraction from methane by photo-activated water was accelerated at the same critical partial pressure of methane, suggesting that the first C–H activation and adsorption of methane was directly assisted by interfacial water.

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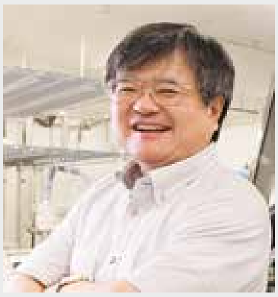
1) N. Aiga and T. Sugimoto, submitted.
2) T. Sugimoto *et al.*, *Nat. Phys.* **12**, 1063–1068 (2016).
3) T. Sugimoto and Y. Matsumoto, *Phys. Chem. Chem. Phys.* **29**, 16435–17012 (2020).
4) H. Sato and T. Sugimoto, *Vac. Surf. Sci.* **63**, 476–481 (2020).
5) H. Sato, T. Higashi, K Takeyasu, A. Ishikawa and T. Sugimoto, submitted.

Organic Solar Cells

Department of Materials Molecular Science
Division of Molecular Functions



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Education

1984	B.E. Osaka University
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Professional Employment

1984	Technical Associate, Institute for Molecular Science
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Awards

2021	Outstanding Achievement Award, Molecular Electronics & Bioelectronics Division, Japan Society of Applied Physics
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2006	Research and Education Award, Osaka University
2004	Editor Award, Japanese Journal of Applied Physics

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Keywords Organic Semiconductors, ppm-Doping, Lateral Junction

Organic solar cells have been intensively studied due to many advantages like flexible, printable, light, low-cost, fashionable, *etc*. Last year, we proposed a novel concept of the structure of organic solar cell, namely, a lateral multilayered junction (Figure 1). An essential point is that the photogenerated holes and electrons are laterally transported and extracted to the respective electrodes. We also investigated the reduction of open-circuit voltage (V_{oc}) loss due to non-radiative recombination in organic solar cells by using high-mobility organic semiconductors. We observed the V_{oc} reaching to thermodynamic (Shockley-Queisser) limit (Figure 2, double red dot). On the other hand, we have been focused on the research on the ppm-level doping effects in organic semiconductor films and organic single crystals for organic solar cells. So far, we have reported complete *pn*-control, doping sensitization, ppm-level doping effects using an extremely low-speed deposition technique reaching 10^{-9} nm s^{-1}, in organic single crystals measured by the Hall effect, which shows a doping efficiency of 24%, and enhancement of open-circuit voltage of organic solar cells by doping. These results can be regarded as a foundation for the construction of high efficient organic solar cells.

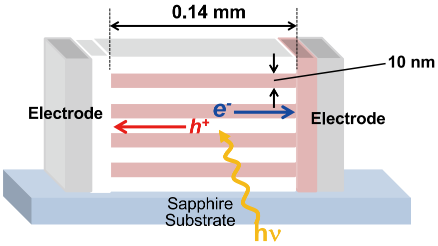

Figure 1. Lateral multilayered junction.

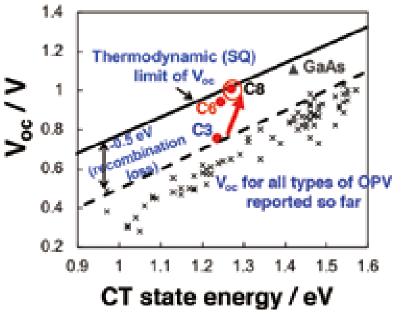

Figure 2. V_{oc} vs. Charge Transfer (CT) state energy of donor/acceptor type organic solar cells. By using high carrier mobility organic semiconductors, V_{oc} reaching SQ-limit was observed (double red dot).

Selected Publications

- M. Kikuchi, M. Hirota, T. Kunawong, Y. Shinmura, M. Abe, Y.Sadamitsu, A. M. Moh, S. Izawa, M. Izaki, H. Naito and M. Hiramoto, "Lateral Alternating Donor/Acceptor Multilayered Junction for Organic Solar Cells," *ACS Appl. Energy Mater.* **2**, 2087–2093 (2019).
- S. Izawa, N. Shintaku, M. Kikuchi and M. Hiramoto, "Importance of Interfacial Crystallinity to Reduce Open-Circuit Voltage Loss in Organic Solar Cells," *Appl. Phys Lett.* **115**, 153301 (2019).
- M. Hiramoto, M. Kikuchi and S. Izawa, "Parts-per-Million-Level Doping Effects in Organic Semiconductor Films and Organic Single Crystals," *Adv. Mater.* **30**, 1801236 (15 pages) (2018). [Invited Progress Report]

1. Efficient Solid-State Photon Upconversion Enabled by Spin Inversion at Organic Semiconductor Interface[1)]

Energy of photons, *i.e.* the wavelength of light, can be upgraded through interactions with materials—a process called photon upconversion (UC). Although UC in organic solids is important for various applications, such as in photovoltaics and bioimaging, conventional UC systems, based on intersystem crossing (ISC), suffer from low efficiency.

In this study, we report a novel UC mechanism at heterojunctions of organic semiconductors in bilayer structures. The UC occurs through spin inversion during the charge separation and recombination at the interface (Figure 3(a)). This spin inversion can efficiently convert the incident photons to triplets without relying on the ISC, whose rate is typically accelerated by the heavy-atom effect. As a result, a solid-state UC system is achieved with an external efficiency of two orders of magnitude higher than those of the conventional systems. Using this result, efficient UC, from near-infrared to visible light, can be realized on flexible organic thin films under a weak light-emitting diode-induced excitation, observable by naked eyes (Figure 3(b)).

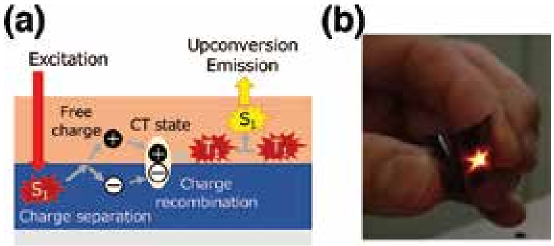

Figure 3. (a) Up-conversion (UC) emission by star-shape patterned NIR LED irradiation. (b) Photographs of UC emission by a star-patterned NIR LED irradiation (750 nm, 71.7 mW/cm^2) on a flexible thin film.

2. Photovoltaic Behavior of Centimeter-Long Lateral Organic Junctions[2)]

Recently, we reported a lateral alternating multilayered junction using a high mobility organic semiconductor.[1)] In this study, we fabricated lateral junction cells having lateral distance (L) reaching cm order (Figure 4(a)). A donor [C8-BTBT (hole mobility: 43 cm^{2}V^{-1}s^{-1})]–acceptor [PTCDI-C8 (electron mobility: 1.7 cm^{2}V^{-1}s^{-1})] combination was used. Buffer layers of BCP and MoO$_3$ were used for the selective carrier collection of electrons and holes, respectively. Surprisingly, even lateral cells with L = 1.8 cm (Figure 4(b)) showed clear photovoltaic behavior (Figure 4(c), red curve). Figure 4(d) shows the L dependence of observed J_{sc} (red curve) and calculated J_{sc} (blue curve) obtained from diffusion lengths of electrons (4.7 mm) and holes (5.5 mm), which are dominated by traps. These diffusion lengths were obtained by the experiments using the moving photomask covering the irradiated surface from respective electrodes. Thus, considerable decrease in photocurrent is attributed to the trap-assisted recombination indicated by the blue curve. A further difference between the observed and calculated curves is due to bimolecular recombination and its effect is small. Thus, we concluded that trap-assisted recombination can be the main reason for photocurrent loss of the long lateral cells. Hence, identifying and removing the defects acting as traps can be done to improve cell performance.

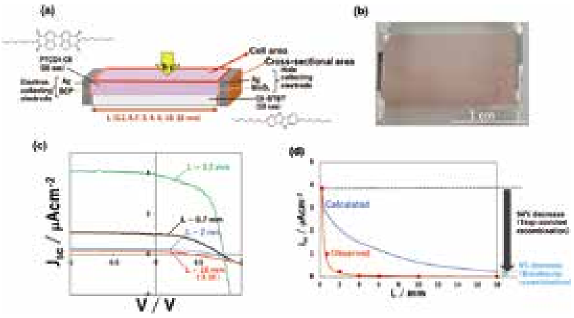

Figure 4. a) Structure of a lateral junction cell. (b) Photograph of a cell with L = 18 mm. (c) J-V curves of cells with L = 0.2, 0.7 and 18 mm. (d) Dependence of short-circuit photocurrent (J_{sc}) on L.

References

1) S. Izawa and M. Hiramoto, *Nat. Photonics*, in press (2021).
2) J. P. Ithikkal, A. Girault, M. Kikuchi, Y. Yabara, S. Izawa and M. Hiramoto, *Appl. Phys Express* **14**, 094001 (2021).

Awards

HIRAMOTO, Masahiro; Outstanding Achievement Award, Molecular Electronics and Bioelectronics Division, Japan Society of Applied Physics (2021).
IZAWA, Seiichiro; The Young Scientist Award, Molecular Electronics and Bio Electronics Division in the Japan Society of Applied Physics (2021).
IZAWA, Seiichiro; Konica Minolta Imaging Science Encouragement Award (2021).
IZAWA, Seiichiro; The Outstanding Presentation Award of the 31st Japan OLED Forum (2021).

Solid-State NMR for Molecular Science

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Award

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Keywords Solid State NMR, Biomolecules, Developments

In order to elucidate functions of molecules, characterization of the molecule is the first step. There is a variety of important molecules, which are insoluble in any solvents and functional at amorphous state. Solid-state NMR enables us to obtain a variety of information at atomic resolution without damage to molecules and significant restrictions. Thus, solid-state NMR is one of the essential tools for the characterizations of those molecules.

We have been working on methodology and hardware developments of solid-state NMR and their application to structural biology and materials science. We study characterization of membrane proteins and peptides, organic materials, natural products and synthetic polymers. Characterization of those molecules based on solid-state NMR is underway through collaborations with several research groups.

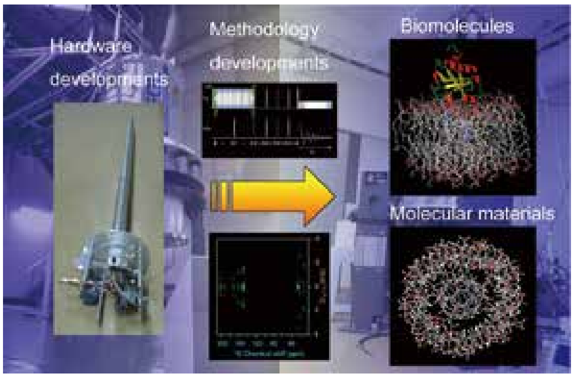

Figure 1. Outline of our studies.

Selected Publications

- N. Uekama, T. Aoki, T. Maruoka, S. Kurisu, A. Hatakeyama, S. Yamaguchi, M. Okada, H. Yagisawa, K. Nishimura and S. Tuzi, "Influence of Membrane Curvature on the Structure of the Membrane-Associated Pleckstrin Homology Domain of Phospholipase C-δ1," *Biochim. Biophys. Acta, Biomembr.* **1788**, 2575–2583 (2009).
- T. Iijima and K. Nishimura, "^{2}H Quadrupolar Carr-Purcell-Meiboom-Gill NMR for Paramagnetic Solids," *Chem. Phys. Lett.* **514**, 181–186 (2011).
- K. Yazawa, F. Suzuki, Y. Nishiyama, T. Ohata, A. Aoki, K. Nishimura, H. Kaji and T. Asakura, "Determination of Accurate ^{1}H Positions of Alanine Tripeptide with Anti-Parallel and Parallel β-Sheet Structures by High Resolution ^{1}H Solid State NMR and GIPAW Chemical Shift Calculation," *Chem. Commun.* **48**, 11199–11201 (2012).
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- M. Yagi-Utsumi, K. Kato and K. Nishimura, "Membrane-Induced Dichotomous Conformation of Amyloid β with the Disordered N-Terminal Segment Followed by the Stable C-Terminal β Structure," *PLoS One* **11**, 0146405 (10 pages) (2016).
- N. Ousaka, F. Mamiya, Y. Iwata, K. Nishimura and E. Yashima, "'Helix-in-Helix' Superstructure Formation through Encapsulation of Fullerene-Bound Helical Peptides within a Helical Poly(methyl methacrylate) Cavity," *Angew. Chem., Int. Ed.* **56**, 791–795 (2017).

1. Structural Characterization of Amyloid-β Protein Oligomer Promoted on Model Neuronal Cell Membranes Using State NMR

Amyloid β (Aβ) protein is disordered in solutions under diluted conditions, however it conforms insoluble amyloid fibrils, which are found in senile plaque as a hallmark of Alzheimer's disease. Although molecular structures of amyloid fibrils have been determined, its molecular process for fibrillation in vivo has not been clarified yet. However, accumulated evidences suggest that the fibrillation process may be promoted on neuronal cell membrane. Especially, it has been reported that Aβ specifically interacts with ganglioside GM1 which is one of the key lipids in lipid raft. Therefore, GM1 embedded into lipid bilayers composed of neutral lipid DMPC may be considered to be the most simplified model neuronal cell membrane. In order to clarify the role of GM1 in the fibrillation process, first, we have successfully determined the oligomeric structure of Aβ (1-40) induced on DMPC bilayers based on solid-state NMR.[1)] We have been collaborated with Prof. Kato group in IMS for those Aβ studies.

In the current study, Aβ (1-40) oligomer induced on model neuronal cell membranes consisting of GM1 and DMPC have been attempted to characterize using solid-state NMR. Based on information of intra- and intermolecular distances and torsion angles of back born obtained from solid-state NMR analyses, precise molecular structure of Aβ oligomer was determined from restrained molecular dynamics simulations in collaboration with Prof. Okumura group in IMS.

The determined Aβ structure conforms disordered N-terminus followed by center and C-terminus β-sheets. Aβ takes intermolecular configuration of antiparallel β-sheet among adjacent molecules, in which different from Aβ fibrils prepared in solution and also Aβ oligomer induced on DMPC bilayers.[1)] Those suggest specific roles of GM1 for the formation of Aβ oligomers. We expect the significant contribution of our determined Aβ oligomer structure to reveal the molecular mechanism of Aβ fibrils on neuronal cell membranes, and thus understanding of Alzheimer's disease. The manuscript of this study is under preparation.

2. Characterizations of Lipid Binding of Prion Fragment Based on Solid-State NMR

"Prion" protein is amyloid protein responsible for class of neurodegenerative diseases such as Bovine spongiform encephalopathy, (BSE), Creutzfeldt-Jakob disease (CJD) of human, scrapie of sheep. Those are collectively known as transmissible spongiform encephalopathies (TSEs). The onset of TSEs has been considered to be arisen by conformational conversion of the native monomeric cellular prion protein (PrPc) into misfolded β-sheet rich form (PrPs), resulting in their insoluble aggregations. Recent studies suggest that those processes are facilitated through interactions with biomembranes, in particular, through binding with ganglioside GM1 in lipid raft. Despite of many studies of prion, molecular mechanism of structural conversion of prion protein and the cytotoxicity have not been clarified yet.

Ultimate goal of this project is provision of molecular basis of prion disease through the characterizations of molecular structure of prion and their interactions with specific lipids based on solid-state NMR analyses. As the first stage, we start study of PrP(106-126) fragment which has been considered as minimum prion fragment to understand their fibrillation mechanism, because of conservations of important properties of formation of amyloid fibrils, membrane binding ability and cytotoxicity. We explore to clarify PrP(106-126) specific binding site in GM1 has been explored through the analyses of chemical shift perturbations of ^{13}C signals from GM1 in POPC/GM1 vesicles from the comparisons of ^{13}C-solid-state NMR spectra in the presence and absence of PrP(106-126). None of ^{13}C signals from POPC exhibited peak shift, but several signals in GM1 exhibited peak shifts due to PrP(106-126) bindings, suggesting specific interactions of Prp(106-126) with GM1 in GM1/POPC lipid bilayers. Further detail is under investigation.

3. Characterization of Protein Using Solid-State NMR

The secretary abundant heat soluble protein (SAHS) from water bear which has ability of torpor under dry-condition, and recovery from torpor by water supply. The biological functions of SAHS at dry-state has not been identified yet, but SAHS has been considered to play key roles during torpor. This is collaboration project with Prof. Kato group in IMS. SAHS consisting of more than 200 amino acid residues and its dry-state is expected to be inhomogeneous. Therefore, in order to investigate structural homogeneity and obtain local conformational information, 2D ^{13}C-homonuclear correlation solid-state NMR measurements were carried out for the dry-state SAHS protein which only isoleucine residues are specifically ^{13}C and ^{15}N isotope labeled. The 6 sets of signals were observed and assigned successfully.

4. Development of Solid-State NMR Probe

We have built a variety of solid-state NMR probes such as static and MAS ^{1}H-X double resonance probes for 400 MHz NMR, and a variable temperature ^{1}H-X double resonance MAS probe for 920 MHz ultra-high field NMR at past. During the past few years, we have been working on building an original solid-state NMR probe which is fully compatible with commercial instruments currently used. Those developed probes were built with originally designed parts except for spinning and spinning rate detection modules which were purchased from NMR company. To replace remained commercial modules, we attempted to design original spinning module. At first stage, two different types of original spinning modules were designed for 4.0 mm sample tube. Those exhibited moderate performances but slightly lower performance respect to commercial module. Based on various tests, we identified the key parts to govern the performance of the spinning. The improved version of spinning module is under developments.

Reference

1) M. Yagi-Utsumi, K. Kato and K. Nishimura, *PLoS One* **11**, 0146405 (10 pages) (2016).

Study on Hydride Ion Conductive Materials for Novel Electrochemical Devices

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Division of Molecular Functions

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Education

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2010	D.S. Tokyo Institute of Technology

Professional Employment

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2011	Assistant Professor, Kanagawa University
2012	JST-PRESTO Researcher (Additional post)
2013	Research Associate Professor, Institute for Molecular Science
2018	Associate Professor, Institute for Molecular Science Associate Professor, The Graduate University for Advanced Studies

Awards

2010	ACerS Spriggs Phase Equilibria Award, American Ceramics Society
2011	Tejima Doctoral Dissertation Award, Tokyo Institute of Technology
2018	The 39th Honda Memorial Young Researcher Award, The Honda Memorial Fundation
2018	The 7th Ishida Award, Nagoya University
2019	Tagawa Solid State Chemistry Awards, Division of Solid State Chemistry, The Electrochemical Society of Japan
2019	Morino Foundation for Molecular Science

Member

Assistant Professor
TAKEIRI, Fumitaka

Graduate Student
OKAMOTO, Kei
UCHIMURA, Tasuku
AYU, Nur Ika Puji*
IZUMI, Yoshiki

Technical Fellow
IMAI, Yumiko
KUBOTA, Akiko

Secretary
KAMIYA, Miho

Keywords Solid State Ionics, H^- Conductor, Battery

Hydrogen has a charge flexibility and can take various charge states such as proton (H^+), atomic hydrogen (H^0), and hydride (H^-) depending on the different bonding states in materials. Due to this feature, whereas hydrogen diffusing in metals behaves a state close to H^0, H^+ becomes the charge carrier in many types of chemical compounds, including polymer, solid acid, MOF, and ceramics. In the former case, hydrogen absorbing alloys and hydrogen embrittlement of metals have been studied, and in the latter case, materials research for fuel cell applications has been actively carried out over the past few decades. In contrast, H^- is a relatively rare state that can only be taken when hydrogen is coordinated to metals with low electronegativity such as alkali metals and was not well recognized as a charge carrier. Therefore, even though H^- has attractive features such as suitability for fast ionic conduction in terms of size, valence, and polarization and strong reduction properties ($E°(H^-/H_2) = -2.35$ V vs. SHE), its electrochemical applications have not been considered. Against this background, we developed a series of H^- conductive oxyhydrides, $La_{2-x-y}Sr_{x+y}LiH_{1-x+y}O_{3-y}$, in 2016 and found its function as an H^- solid electrolyte for the first time. Based on the results, our group is challenging the progress of materials science on H^- conductors and the development of novel electrochemical devices utilizing H^-conduction phenomena.

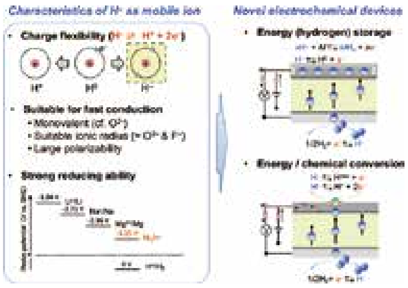

Figure 1. Our research concept toward realization of electrochemical devices utilizing hydrogen charge flexibility.

Selected Publications

- G. Kobayashi, Y. Hinuma, S. Matsuoka, A. Watanabe, M. Iqbal, M. Hirayama, M. Yonemura, T. Kamiyama, I. Tanaka and R. Kanno, *Science* **351**, 1314–1317 (2016).
- A. Watanabe, G. Kobayashi, N. Matsui, M. Yonemura, A. Kubota, K. Suzuki, M. Hirayama and R. Kanno, *Electrochemistry* **85(2)**, 88–92 (2017).
- F. Takeiri, A. Watanabe, A. Kuwabara, H. Nawaz, N. Ayu, M. Yonemura, R. Kanno and G. Kobayashi, *Inorg. Chem.* **58**, 4431–4436 (2019).
- N. Matsui, G. Kobayashi, K. Suzuki, A. Watanabe, A. Kubota, Y. Iwasaki, M. Yonemura, M. Hirayama and R. Kanno, *J. Am. Ceram. Soc.* **102**, 3228–3235 (2019).
- H. Nawaz, F. Takeiri, A. Kuwabara and M. Yonemura and G. Kobayashi, *Chem. Commun.* **56**, 10373–10376 (2020).
- T. Uchimura, F. Takeiri, K. Okamoto, T. Saito, T. Kamiyama and G. Kobayashi, *J. Mater. Chem. A* **9**, 20371–20374 (2021).

1. Study on H$^-$ Conductive Oxyhydrides[1–3]

In 2016, we synthesized a series of K_2NiF_4-type oxyhydrides, $La_{2-x-y}Sr_{x+y}LiH_{1-x+y}O_{3-y}$ (LSLHO), which are equipped with anion sublattices that exhibit flexibility in the storage of H$^-$, O^{2-}, and vacancies (Figure 2 upper) and demonstrated pure H$^-$ conduction properties in the oxyhydrides.[1] The Li-based oxyhydrides acted as solid electrolytes and the all-solid-state Ti/LSLHO/TiH_2 cell showed a redox reaction based on hydrogen storage/desorption on the electrodes, which is a first battery reaction using H$^-$ conduction phenomena.

More recently, we synthesized novel H$^-$ conductive oxyhydrides, Ba_2MHO_3 (M = Sc, Y),[2,3] with the K_2NiF_4-type structure and confirmed its unique site selectivity for H$^-$. In accordance with the electrostatic valence rule, it was found that the hydride ions in Ba_2MHO_3 selectively occupied the rock-salt layer, in contrast to those of the observed isostructural Li- based oxyhydrides that preferentially occupy the perovskite layer (Figure 2). The cation size at the octahedral center influences the anion arrangement within the rock salt layer, and in the Y-oxyhydride, the complete ordering of H/O led to the formation of the [Ba_2H_2] layers. These results indicate that anion ordering in oxyhydrides could be tuned by appropriate element substitutions, which is a new insight for designing H$^-$ conducting materials.

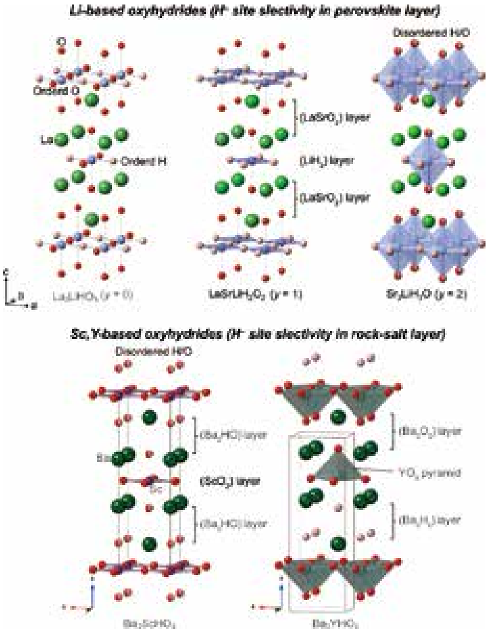

Figure 2. Crystal structures of H$^-$ conductive oxyhydrides $La_{2-x-y}Sr_{x+y}LiH_{1-x+y}O_{3-y}$ ($x = 0$, $y = 0, 1, 2$) and Ba_2MHO_3 (M = Sc, Y).

2. Materials Processing of Oxyhydrides for Electrochemical Applications[4–6]

Synthesizing oxyhydrides usually requires unique methods such as solid-state reactions at high-pressure and topochemical reactions using CaH_2 reductant. Since the former method is a sealed reaction system, loss of light elements, such as hydrogen, can be prevented, making it a suitable synthesis method for composition control and, ultimately, exploration for new materials. On the other hand, the latter is an O^{2-}/H$^-$exchange reaction using oxides as precursors and is useful for preparing metastable phases that the conventional sintering process cannot obtain. However, the low synthesis volume in the high-pressure method and less reproducibility of composition due to complicated multi-step processes such as washing in CaH_2 reduction have prevented expanding the study on oxyhydrides to applicable research for electrochemical devices. To resolve the above problems, we have been trying to establish a suitable synthesis method for oxyhydrides.

For Li-based oxyhydrides (LSLHO) with the K_2NiF_4-type structure, we have successfully established the solid-state reaction method under ambient-pressure.[4,5] Electromotive force measurements using hydrogen concentration cells became possible by preparing the LSLHO sintered pellets with sufficient size.

We have also succeeded in direct synthesis of barium titanium oxyhydride $BaTiO_{3-x}H_x$ by mechanochemical reaction, allowing gram-scale and speedy preparation of the functional material. Its unique reaction condition without external heating might be suitable for materials exploration of oxyhydrides. We also confirmed that the prepared polycrystalline $BaTiO_{3-x}H_x$ worked as a hydrogen-permeable electrode. This result suggests that H$^-$/e$^-$ mixed conducting oxyhydrides are promising for electrode use in electrochemical chemical/ energy conversion devices (Figure 3).[6]

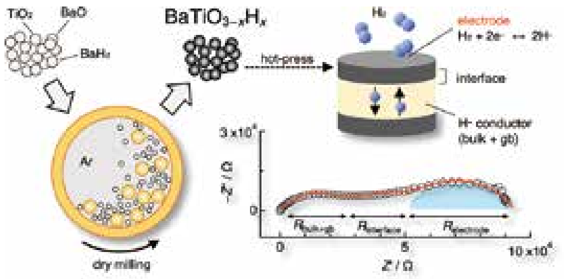

Figure 3. $BaTiO_{3-x}H_x$ synthesized by a mechanochemical method and its performance as hydrogen permeable electrodes.

References

1) G. Kobayashi* *et al.*, *Science* **351**, 1314–1317 (2016).
2) F. Takeiri, G. Kobayashi* *et al.*, *Inorg. Chem.* **58**, 4431–4436 (2019).
3) H. Nawaz, G. Kobayashi* *et al.*, *Chem. Commun.* **56**, 10373–10376 (2020).
4) A. Watanabe, G. Kobayashi* *et al.*, *Electrochemistry* **85**, 88–92 (2017).
5) N. Matsui, G. Kobayashi* *et al.*, *J. Am. Ceram. Soc.* **102**, 3228–3235 (2019).
6) T. Uchimura, G. Kobayashi* *et al.*, *J. Mater. Chem. A* **9**, 20371–20374 (2021).

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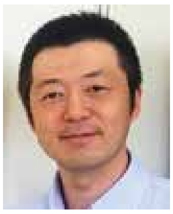
* carrying out graduate research on Cooperative Education Program of IMS with High Energy Accelerator Research Organization

Clarification of the Energy Conversion Mechanism at the Surface and Interface by Scanning Probe Microscopy

Instrument Center



MINATO, Taketoshi
Senior Researcher

At the interface between solid and liquid, energy conversion reactions in the physical, chemical, and biological process proceed. The details of such a energy conversion process is yet to be clarified completely.[1,2] Scanning probe microscopy (SPM) is a powerful method to clarify such mechanisms because it can explore structural, mechanical, electric and electronic properties in atomic (or molecular) scales. As shown in an atomic resolved SPM image of $CaCO_3(104)$ surface in 5 mM NaCl aqueous solution (Figure 1), atomic scale properties are investigated by SPM.

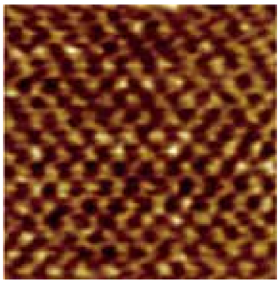


Figure 1. An atomically resolved friction image of $CaCO_3(104)$ surface in 5 mM NaCl aqueous solution. image size: 5 nm × 5 nm.

Rechargeable battery plays an important role in the development of new systems of energy storage and transfer. Currently, lithium-ion batteries have been widely used for energy systems. Recent demands for rechargeable batteries require more developments in the capacity, cyclic performance and lifetime. For these developments, the clarification of the reaction mechanism at the interface between electrode and electrolyte during the charge and discharge reactions is crucial.

During the charge and discharge reactions of rechargeable battery, solvent, carrier ions, additive and solute produce specific states at the interface between electrode and electrolyte. The interface states are believed to change the physical properties depending on the potential and strongly correlate the battery performances. However, detecting the interface states is challenging. By setting up SPM system which can operate in electrochemical conditions, we detected and the investigated physical properties of interface states. Figure 2 shows force curves obtained at the interface between organic electrolyte for lithium-ion battery and gold electrode. The force curve was changed by the sample potential between +1.0 (blue) and −1.0 V (red) (vs Pt). The changes of the force curves were caused by the interface states, exhibiting the evidence of the formation of the thick interface states by electrolyte at −1.0 V. By the analysis of the force curves, the mechanical properties of the interface states were also clarified. The analysis of the electrode/electrolyte interface will be applied to innovative battery systems[3–5] that can overcome current battery performances.

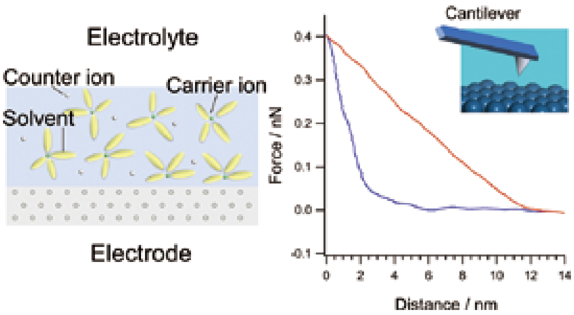


Figure 2. A schematic model of electrode/electrolyte interface in a rechargeable battery and force curves obtained by electrochemical SPM systems at the interface between organic electrolyte for lithium-ion battery and gold electrode with changing the sample potential. The blue and red curve were obtained at +1.0 and −1.0 V (vs. Pt), respectively. The force curves were measured during the approaching the tip to the interface. The distance was determined from the point detecting 0.4 nN.

References

1) T. Minato and T. Abe, *Prog. Surf. Sci.* **92**, 240–280 (2017).
2) T. Minato, K.-i. Umeda, K. Kobayashi, Y. Araki, H. Konishi, Z. Ogumi, T. Abe, H. Onishi and H. Yamada, *Jpn. J. Appl. Phys.* (review), **60**, SE0806 (2021).
3) T. Minato, H. Konishi, A. Celik Kucuk, T. Abe and Z. Ogumi, *Ceramics Japan* **54**, 637 (2019).
4) H. Nakano, T. Matsunaga, T. Mori, K. Nakanishi, Y. Morita, K. Ide, K.-i. Okazaki, Y. Orikasa, T. Minato, K. Yamamoto, Z. Ogumi and Y. Uchimoto, *Chem. Mater.* **33**, 459–466 (2021).
5) K. Shimoda, T. Minato, H. Konishi, G. Kano, T. Nakatani, S. Fujinami, A. C. Kucuk, S. Kawaguchi, Z. Ogumi and T. Abe, *J. Electroanal. Chem.* **895**, 115508 (2021).

Visiting Professors

Visiting Professor
KISHINE, Jun-ichiro *(from The Open University of Japan)*

Theoretical Studies on Chiral Material Science

The concept of chirality is ubiquitous in natural sciences. However, until only recently, research fields on chirality had been fragmented into separated branches of physics, chemistry and biology. Even inside physics, a term "chiral" has been used in different meanings in condensed matter and high-energy physics. One of the most important mission of our project is to integrate the scattered concepts of chirality and make a roadmap toward an attempt at synthesis of chiral material sciences. Let us remind the Laurence Barron's definition of the true chirality, *i.e.*, true chirality is shown by systems existing in two distinct enantiomeric states that are interconverted by space inversion, but not by time reversal combined with any proper spatial rotation. The space inversion is a matter of geometrical symmetry, while time reversal is a matter of dynamical motion. This unambiguous definition clearly indicates that the concept of chirality ties geometry and dynamics. Conversion of geometry into dynamics naturally leads to material functionalities. The main purpose of this research project is to integrate these concepts in a unified manner. During this one year, we have focused on theoretical description of the chirality-induced phonon in non-centrosymmetric crystals.

Visiting Associate Professor
FURUKAWA, Ko *(from Niigata University)*

Advanced ESR Study of Molecule-Based Functional Materials

To develop the high-efficiency molecule-based device, it's vital to clarify the mechanism of the functional molecules/materials. We investigate the mechanism of the solid-state functional materials in terms of advanced electron spin resonance (ESR) spectroscopy such as high-field/high-frequency ESR, time-resolved ESR, pulsed-ESR and so on. Recently, our themes are following three (I) spin dynamics study of molecule-based materials with the complex function combined to photoconductivity and photo-induced magnetic properties, (II) operand ESR study of the novel oxygen reduction reaction (ORR) catalyst for fuel cell, and (III) the soil environments were investigated by using ESR spectroscopy for the vegetable food such as the rice and tea leaves.

Visiting Associate Professor
OSHIMA, Yugo *(from RIKEN)*

Development of ESR Probe for Molecular Field-Effect Transistor (FET) Devices

Recently, a novel type of ferromagnet (Et-4BrT)[Ni(dmit)$_2$]$_2$ has been developed by Kusamoto Group and Yamamoto Group in IMS (dmit is 1,3-dithiol-2-thiole-4,5-dithiolate and Et-4BrT is ethyl-4-bromothiazolium). We have found that this ferromagnet is the first realization of the Nagaoka-Penn ferromagnetism, where the ferromagnetism is achieved by the light hole-doping of the insulating Ni(dmit)$_2$ layer owing to the internal dipole moment of the monovalent cation Et-4BrT (*Sci. Rep.* **11**, 1332 (2021)). Our latest interest is whether the ferromagnetism of this material can be controlled by electrical doping or not. In collaboration with Yamamoto Group, we have newly developed an ESR sample holder for field-effect transistors (FETs), so that we can control precisely the electrical doping of (Et-4BrT)[Ni(dmit)$_2$]$_2$ by means of FET structure. We will investigate the magnetic properties of (Et-4BrT)[Ni(dmit)$_2$]$_2$ by carrier doping from ESR spectroscopy.

RESEARCH ACTIVITIES

Life and Coordination-Complex Molecular Science

Department of Life and Coordination-Complex Molecular Science is composed of two divisions of biomolecular science, two divisions of coordination-complex molecular science, and one adjunct division. Biomolecular science divisions cover the studies on functions, dynamic structures, and mechanisms for various biomolecules such as sensor proteins, metalloproteins, biological-clock proteins, glycoconjugates, antibodies, and motor proteins. Coordination-complex divisions aim to develop molecular catalysts and functional metal complexes for transformation of organic molecules, and molecular materials with photonic-electronic-magnetic functions and three-dimensional complex structures. Interdisciplinary alliances in this department aim to create new basic concepts for the molecular and energy conversion through the fundamental science conducted at each division.

Bioinorganic Chemistry of Metalloproteins Responsible for Metal Homeostasis and Signal Sensing

Department of Life and Coordination-Complex Molecular Science
Division of Biomolecular Functions

AONO, Shigetoshi
Professor
[aono@ims.ac.jp]

Education

1982 B.S. Tokyo Institute of Technology
1987 Ph.D. Tokyo Institute of Technology

Professional Employment

1988 Postdoctoral Fellow, Georgia University
1989 Assistant Professor, Tokyo Institute of Technology
1994 Associate Professor, Japan Advanced Institute of Science and Technology
2002 Professor, Institute for Molecular Science
Professor, Okazaki Institute for Integrative Bioscience (–2018)
Professor, The Graduate University for Advanced Studies
2018 Professor, Exploratory Research Center on Life and Living Systems (ExCELLS)

Member

Assistant Professor
MURAKI, Norifumi
IMS Research Assistant Professor
TAKEDA, Kouta
Post-Doctoral Fellow
NAM, Dayeon
TOHDA, Rei
Technical Fellow
MURAKI, Megumi
Secretary
NAKANE, Kaori

Keywords Bioinorganic Chemistry, Metalloproteins, Sensor Protein

Transition metal ions and metalloproteins play crucial roles in meeting the energy demands of the cell by playing roles in intermediary metabolism and in signal transduction processes. Although they are essential for biological function, metal ion bioavailability must be maintained within a certain range in cells due to the inherent toxicity of all metals above a threshold. This threshold varies for individual metal ions. Homeostasis of metal ions requires a balance between the processes of uptake, utilization, storage, and efflux and is achieved by the coordinated activities of a variety of proteins including extracytoplasmic metal carriers, ion channels/pumps/transporters, metal-regulated transcription and translation proteins, and enzymes involved in the biogenesis of metal-containing cofactors/metalloproteins. In order to understand the processes underlying this complex metal homeostasis network, the study of the molecular processes that determine the protein-metal ion recognition, as well as how this event is transduced into a functional output, is required. My research interests are focused on the elucidation of the structure and function relationships of metalloproteins responsible for the regulation of biological homeostasis.

I am also working on gas sensor proteins. Gas molecules such as O_2, NO, CO and ethylene are present in the environment and are endogenously (enzymatically) produced to act as signaling molecules in biological systems. Sensing these gas molecules is the first step in their acting as signaling molecules. Sensor proteins are usually required. Input signals generated by gas sensing have to transduce to output signals that regulate biological functions. This is achieved by biological signal-transduction systems. Recognition of the cognate gas molecules is a general mechanism of functional regulation for gas sensor proteins. This induces conformational changes in proteins that controls their activities for following signal transductions. Interaction between gas molecules and sensor proteins is essential for recognition of gas molecules. Metal-containing prosthetic groups are widely used. In my research group, our research focuses on transition metal-based gas-sensor proteins and the signaling systems working with them.

Selected Publications

- M. Nishinaga, H. Sugimoto, Y. Nishitani, S. Nagai, S. Nagatoishi, N. Muraki, T. Tosha, K. Tsumoto, S. Aono, Y. Shiro and H. Sawai, "Heme Controls the Structural Rearrangement of Its Sensor Protein Mediating Bacterial Survival," *Commun. Biol.* **4**, 467 (12 pages) (2021).
- N. Muraki, K. Takeda, D. Nam, M. Muraki and S. Aono, "Structural Characterization of Thermoglobin from a Hyperthermophilic Bacterium *Aquifex aeolicus*," *Chem. Lett.* **50**, 603–606 (2021).
- N. Muraki, C. Kitatsuji, Y. Okamoto, T. Uchida, K. Ishimori and S. Aono, "Structural Basis for Heme Transfer Reaction in Heme Uptake Machinery from Corynebacteria," *Chem. Commun.* **55**, 13864–13867 (2019).
- N. Muraki, K. Ishii, S. Uchiyama, S. G. Itoh, H. Okumura and S. Aono, "Structural Characterization of HypX Responsible for CO Biosynthesis in the Maturation of NiFe-Hydrogenase," *Commun. Biol.* **2**, 385 (12 pages) (2019).
- A. Pavlou, H. Yoshimura, S. Aono and E. Pinakoulaki, "Protein Dynamics of the Sensor Protein HemAT as Probed by Time-Resolved Step-Scan FTIR Spectroscopy," *Biophys. J.* **114**, 584–591 (2018).
- A. Pavlou, A. Loullis, H. Yoshimura, S. Aono and E. Pinakoulaki, "Probing the Role of the Heme Distal and Proximal Environment in Ligand Dynamics in the Signal Transducer Protein HemAT by Time-Resolved Step-Scan FTIR and Resonance Raman Spectroscopy," *Biochemistry* **56**, 5309–5317 (2017).

1. Structural Characterization of Thermoglobin from a Hyperthermophilic Bacterium *Aquifex aeolicus*

Globins are heme-binding proteins, which show a variety of biological functions such as oxygen transport, oxygen storage, redox catalysis and gas sensing. In bacteria, four distinct globins are identified; single domain hemoglobin (sdHb), truncated hemoglobin (tHb), flavohemoglobin (fHb) and globin-coupled sensor (GCS). Truncated hemoglobins (tHbs) are shorter than the canonical vertebrate hemoglobins by 20–40 residues. Whereas the canonical hemoglobins, sdHb, fHb and GCS are composed of eight α-helices (A–H), that fold into a 3-on-3 α-helical sandwich structure, tHbs form a 2-on-2 α-helical sandwich in which helices B and E lie over helices G and H. The physiological function of some sdHb, tHb, and fHb is proposed to provide resistance to nitrosative stress such as reactive nitrogen species. In this work, the structural characterization of AaTgb was carried out by X-ray crystallography.

We have determined the crystal structure of Y29F-AaTgb in the imidazole-bound form. Y29F-AaTgb shares the structural similarity to known bacterial sdHb structures; *Campylobacter jejuni* Hb (CjHb, 44% sequence identity), *Methylacidiphilum infernorum* Hb known as hell's gate globin I (HGbI, 32% sequence identity) and *Vitreoscilla stercoraria* Hb (VsHb, 43% sequence identity). sdHb was discovered from *Vitreoscilla stercoraria*, which shares approximately 30% amino acid sequence identity with the globin domain of fHb that functions as nitric oxide dioxygenase. Based on the amino acid sequence homology, it is assumed that sdHb also acts as nitric oxide dioxygenase. Indeed, *Campylobacter jejuni* Hb and *Helicobacter pullorum* Hb have been reported to contribute to remove nitric oxide.

The superposition between the Cα atoms of Y29F-AaTgb and CjHb (PDB ID: 2wy4), HGbI (PDB ID: 3s1i) and VsHb (PDB ID: 3vhb) shows a root mean square deviation of 0.89 Å, 1.04 Å and 1.18 Å, respectively. By using a structural homology search in Structure Navigator in PDBj, Y29F-AaTgb has the highest structural homology to the globin domain of nitric oxide dioxygenase from *Rhodothermus marinus* (RmaNOD, UniProt ID: D0MGT2). The superposition between the Cα atoms of Y29F-AaTgb and the globin domain of RmaNOD (PDB ID: 6wk3) shows a root mean square deviation of 0.60 Å with 48% sequence identity. The structural similarity of AaTgb to sdHb and RmaNOD suggests a possibility that AaTgb is also responsible for NO detoxification, though further studies must be required to confirm this hypothesis.

The heme environmental structure of Y29F-AaTgb is shown in Figure 1. In Y29F-AaTgb, the heme iron is coordinated by His82 and imidazole in the proximal and distal side, respectively. The distances between iron and nitrogen atom are 2.17 and 2.13 Å for His82 and imidazole, respectively. ND1 of His82 forms hydrogen bonds with OH of Tyr92 and OE2 of Glu132. These hydrogen bonds will fix the orientation of imidazole ring of His82. These amino acids and hydrogen bonds network in the proximal site are conserved in sdHbs except to HGbI.

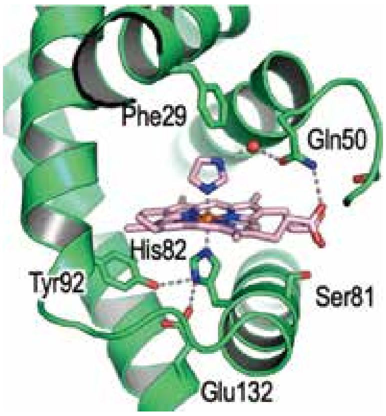


Figure 1. Heme environmental structure of Y29F-AaTgb in the imdazole-bound form. Hydrogen bonds are shown in dashed lines. Nitrogen and oxygen atoms are shown in blue and red, respectively. Red sphere in the heme pocket shows the water molecule W.

Imidazole bound to heme participate in a hydrogen bonding network in the distal heme pocket. A well-defined water molecule (W) present in the distal heme pocket forms hydrogen bonds with imidazole and Gln50. Gln50 forms a hydrogen bond with a propionate group of heme. This hydrogen bonding network will stabilize and fix the orientation of imidazole ligand. On the other hand, Phe29 was 3.41 Å from nitrogen of imidazole and 3.69 Å from the water molecule W.

The binding affinity of imidazole (K_d) to the ferric form of AaTgb was 4.1 and 5.7 μM for the wild type and Y29F variant, respectively, which were determined by measuring absorbance changes upon imidazole titration. Similar binding affinity of imidazole will be achieved as a loss of the hydrogen bond between Tyr29 and imidazole in Y29F variant is compensated by the hydrogen bond between the water molecule W and imidazole.

2. Structural and Functional Analyses of Heme Sensing Transcriptional Regulator PefR

Hemes (iron-porphyrins) are critical for biological processes in all organisms. In this work, structural, functional and spectroscopic analyses of the heme-responsive sensor protein PefR from *Streptococcus agalactiae*, were carried out to elucidate the molecular mechanisms of how heme molecule regulates the functional acitivity of PefR. The crystal structures of apo-PefR, apo-PefR/DNA complex, and heme-bound (holo-) PefR were determined at 2.6, 2.5 Å, and 1.7 Å resolutions, respectively. Structural comparison of the apo-PefR/DNA complex and holo-PefR reveals that conformational change occur around the heme-binding site, which is induced by the coordination of His114 of one subunit to heme followed by the coordination of the N-terminal amino group of the other subunit. Rigid-body motion of the α1 helix in association with heme accommodation alters the relative orientation of the DNA-binding domain in holo-PefR from the apo form, resulting in a conformational change in the DNA-binding domain.

Dynamical Ordering of Biomolecular Systems for Creation of Integrated Functions

Department of Life and Coordination-Complex Molecular Science
Division of Biomolecular Functions

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Director, ExCELLS

Education

1986	B.S. The University of Tokyo
1991	Ph.D. The University of Tokyo

Professional Employment

1991	Assistant Professor, The University of Tokyo
1997	Lecturer, The University of Tokyo
2000	Professor, Nagoya City University
2008	Professor, Institute for Molecular Science Professor, Okazaki Institute for Integrative Bioscience (–2018) Professor, The Graduate University for Advanced Studies
2006	Visiting Professor, Ochanomizu University
2013	Project Leader, JSPS Grant in Aid for Scientific Research on Innovative Areas “Dynamical Ordering of Biomolecular Systems for Creation of Integrated Functions”
2018	Professor, Exploratory Research Center on Life and Living Systems (ExCELLS)

Awards

2000	The Pharmaceutical Society of Japan Award for Young Scientists
2011	The Pharmaceutical Society of Japan Award for Divisional Scientific Promotions
2011	The 48th Baelz Prize

Member

Assistant Professor
  YAGI-UTSUMI, Maho
  YANAKA, Saeko
Graduate Student
  HIRANYAKORN, Methanee
  SEKIGUCHI, Taichiro
  YUNOKI, Yasuhiro*
  YOGO, Rina*
  SAITO, Taiki*
  UMEZAWA, Fumiko*
  SASAKI, Yudai*
  YAMADA, Rino*
  NISHIMURA, Seiji*
  SHIN, Kana*
Technical Fellow
  ISONO, Yukiko
Secretary
  FUKUTOMI, Yukie

Keywords Biomolecule Organization, NMR

Living systems are characterized as dynamic processes of assembly and disassembly of various biomolecules that are self-organized, interacting with the external environment. The omics-based approaches developed in recent decades have provided comprehensive information regarding biomolecules as parts of living organisms. However, fundamental questions still remain unsolved as to how these biomolecules are ordered autonomously to form flexible and robust systems (Figure 1). Biomolecules with complicated, flexible structures are self-organized through weak interactions giving rise to supramolecular complexes that adopt their own dynamic, asymmetric architectures. These processes are coupled with expression of integrated functions in the biomolecular systems.

Toward an integrative understanding of the principles behind the biomolecular ordering processes, we conduct multidisciplinary approaches based on detailed analyses of dynamic structures and interactions of biomolecules at atomic level, in conjunction with the methodologies of molecular and cellular biology along with synthetic and computational technique.

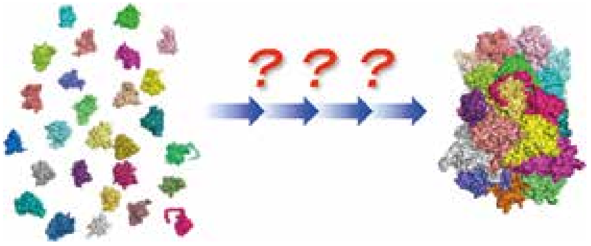

Figure 1. Formation of supramolecular machinery through dynamic assembly and disassembly of biomolecules.

Selected Publications

- H. Yagi, S. Yanaka and K. Kato, “Structural and Functional Roles of the *N*-Glycans in Therapeutic Antibodies,” in *Comprehensive Glycoscience, 2nd edition*, J. Barchi, Ed., Elsevier; Oxford, **vol. 5**, pp. 534–542 (2021).
- S. Yanaka, R. Yogo and K. Kato, “Biophysical Characterization of Dynamic Structures of Immunoglobulin G,” *Biophys. Rev.* **12**, 637–645 (2020).
- T. Satoh and K. Kato, “Structural Aspects of ER Glycoprotein Quality-Control System Mediated by Glucose Tagging,” in *Glycobiophysics*, Y. Yamaguchi and K. Kato, Eds., Springer Nature; Singapore, pp. 149–169 (2018).
- K. Kato, H. Yagi and T. Yamaguchi, “NMR Characterization of the Dynamic Conformations of Oligosaccharides,” in *Modern Magnetic Resonance, 2nd Edition*, G. A. Webb, Ed., Springer International Publishing, pp. 737–754 (2018).
- T. Yamaguchi and K. Kato, “Molecular Dynamics of Gangliosides,” in *Gangliosides*, S. Sonnino and A. Prinetti, Eds., Methods in Molecular Biology, Humana Press; New York, **vol. 1804**, pp. 411–417 (2018).
- K. Kato and T. Satoh, “Structural Insights on the Dynamics of Proteasome Formation,” *Biophys. Rev.* **10**, 597–604 (2018).

1. Methodological Advancements for Analysis of Conformational Dynamics and Interactions of Biomolecules

During the past year, we have made significant progresses in our methods for investigating conformational dynamics and interactions of biomolecules, especially oligosaccharides and glycoproteins. Oligosaccharides play versatile roles in various biological systems but are difficult to characterize from a structural viewpoint due to their remarkable degrees of freedom in internal motion. Therefore, molecular dynamics simulations have been widely used to delineate the dynamic conformations of oligosaccharides. However, hardly any methods have thus far been available for the comprehensive characterization of simulation-derived conformational ensembles of oligosaccharides. We developed a theoretical approach for comprehensive characterization of oligosaccharide conformational ensembles with conformer classification by free-energy landscape via reproductive kernel Hilbert space.1) This methodology will open opportunities to explore oligosaccharides' conformational spaces, and more generally, molecules with high degrees of motional freedom.

In addition, we sophisticated our experimental methods for stable-isotope-assisted measurements of nuclear magnetic resonance (NMR) and small-angle neutron scattering (SANS) using immunoglobulin G (IgG) as a model glycoprotein. This enabled us to achieve NMR spectral assignments of the N-linked oligosaccharides as well as polypeptide backbones of the Fc portion of IgG.2,3) Moreover, we combined inverse contrast-matching SANS method with size exclusion chromatography and thereby successfully observed SANS from the non-deuterated IgG glycoprotein in complex with its binding partners with 75% deuteration, which were unobservable in terms of SANS in D_2O.4) Furthermore, we revealed residual structure of unfolded ubiquitin by employing a dimethylsulfoxide-quenched hydrogen/deuterium-exchange NMR technique with the use of spin desalting columns.5)

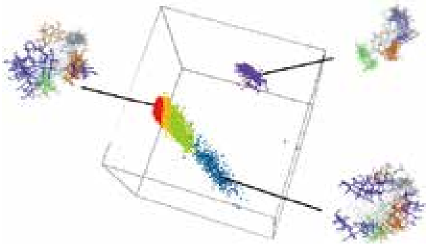

Figure 2. A kernel method for the comprehensive characterization of conformational ensembles of oligosaccharides in association with the conformational free-energy landscape.

2. Integrative Approaches for Characterizing Biomolecular Assembly Systems

We characterized various biomolecular assembling systems using integrative approaches. Cold atmospheric plasma (CAP) has attracted much attention in the fields of biotechnology and medicine owing to its potential utility in clinical applications. Recently accumulating evidence has demonstrated that CAP influences protein structures. However, there remain open questions regarding the molecular mechanisms behind the CAP-induced structural perturbations of biomacromolecules. In view of this situation, we investigated the potential effects of CAP irradiation of amyloid β (Aβ).6) Based on NMR, mass spectrometry, and kinetics analyses, we demonstrated that the CAP irradiation results in selective oxidation of the methionine residue at position 35 of Aβ, which suppresses amyloid fibril formation. This modification is made by H_2O_2 generated in the plasma-irradiated buffer solution, rather than by the direct action of the plasma.

We also conducted a cryo-electron microscopic study of the proteasome α7 subunit, which self-assembles into a homo-tetradecamer consisting of two layers of α7 heptameric rings.7) Our observations suggest that the α7 double-ring structure was significantly different from the previously reported crystallographic model and fluctuates considerably in solution.

In addition, we contributed to an IMS Joint Research lead by Dr. Ryo Ohtani (Kyushu University) on two-dimensional coordination polymers as *pseudo-membrane jackets*, which achieve visible phase separation in cell membrane.8,9) This system opens new avenues for the application of metal complex lipids toward controlling lipid distributions in fluid membranes.

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6) M. Yagi-Utsumi *et al.*, *Int. J. Mol. Sci.* **22**, 3116 (2021).
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9) R. Ohtani *et al.*, *Angew. Chem., Int. Ed.* **59**, 17931–17937 (2020).

Awards

YAGI-UTSUMI, Maho; 10th Young Researcher Award, National Institutes of Natural Sciences (2021).
YANAKA, Saeko; Award for Young Scientists, the Division of Physical Sciences of the Pharmaceutical Society of Japan (2021).
UMEZAWA, Fumiko; Young Scientist Award, Japanese Biochemical Society Chubu Branch (2021).
SAITO, Taiki; the Young Scientist Award, the 16th Forum of the Glycoscience Base for Chubu (2021).

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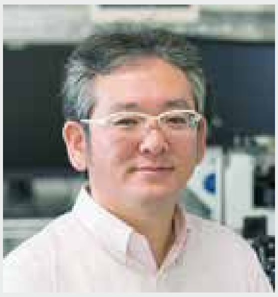
* carrying out graduate research on Cooperative Education Program of IMS with Nagoya City University

Operation and Design Principles of Biological Molecular Machines

Department of Life and Coordination-Complex Molecular Science
Division of Biomolecular Functions



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Keywords Molecular Motors, Single-Molecule Analysis, Protein Engineering

Activity of life is supported by various molecular machines made of proteins. Protein molecular machines are tiny, but show very high performance, and are superior to man-made machines in many aspects. One of the representatives of protein molecular machines is linear and rotary molecular motors (Figure 1). Molecular motors generate mechanical forces and torques that drive their unidirectional motions from the energy of chemical reaction or the electrochemical potential across the cell membrane.

We unveil operation principles of molecular motors with advanced single-molecule functional analysis. With the help of site-saturation mutagenesis and robot-based automation, we also engineer non-natural molecular motors to understand their design principles.

Figure 1. Protein molecular machines. (Left) A linear molecular motor chitinase A. (Center and Right) Rotary molecular motors F$_1$-ATPase and V$_1$-ATPase, respectively.

Selected Publications

- A. Visootsat, A. Nakamura, P. Vignon, H. Watanabe, T. Uchihashi and R. Iino, "Single-Molecule Imaging Analysis Reveals the Mechanism of a High-Catalytic-Activity Mutant of Chitinase A from *Serratia marcescens*," *J. Biol. Chem.* **295**, 1915–1925 (2020).
- J. Ando, T. Shima, R. Kanazawa, R. Shimo-Kon, A. Nakamura, M. Yamamoto, T. Kon and R. Iino, "Small Stepping Motion of Processive Dynein Revealed by Load-Free High-Speed Single-Particle Tracking," *Sci. Rep.* **10**, 1080 (2020).
- J. Ando, A. Nakamura, M. Yamamoto, C. Song, K. Murata and R. Iino, "Multicolor High-Speed Tracking of Single Biomolecules with Silver, Gold, Silver-Gold Alloy Nanoparticles," *ACS Photonics* **6**, 2870–2883 (2019).
- T. Iida, Y. Minagawa, H. Ueno, F. Kawai, T. Murata and R. Iino, "Single-Molecule Analysis Reveals Rotational Substeps and Chemo-Mechanical Coupling Scheme of *Enterococcus hirae* V$_1$-ATPase," *J. Biol. Chem.* **294**, 17017–17030 (2019).
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1. Domain Architecture Divergence Leads to Functional Divergence in Binding and Catalytic Domains of Bacterial and Fungal Cellobiohydrolases[1)]

Cellobiohydrolases directly convert crystalline cellulose into cellobiose and are of biotechnological interest to achieve efficient biomass utilization. As a result, much research in the field has focused on identifying cellobiohydrolases that are very fast. Cellobiohydrolase A from the bacterium *Cellulomonas fimi* (CfCel6B) and cellobiohydrolase II from the fungus *Trichoderma reesei* (TrCel6A) have similar catalytic domains (CDs) and show similar hydrolytic activity. However, TrCel6A and CfCel6B have different cellulose-binding domains (CBDs) and linkers: TrCel6A has a glycosylated peptide linker, whereas CfCel6B's linker consists of three fibronectin type 3 domains. We previously found that TrCel6A's linker plays an important role in increasing the binding rate constant to crystalline cellulose. However, it was not clear whether CfCel6B's linker has similar function. Here we analyze kinetic parameters of CfCel6B using single-molecule fluorescence imaging to compare CfCel6B and TrCel6A. We find that CBD is important for initial binding of CfCel6B, but the contribution of the linker to the binding rate constant or to the dissociation rate constant is minor. The crystal structure of the CfCel6B CD showed longer loops at the entrance and exit of the substrate-binding tunnel compared with TrCel6A CD, which results in higher processivity. Furthermore, CfCel6B CD showed not only fast surface diffusion but also slow processive movement, which is not observed in TrCel6A CD. Combined with the results of a phylogenetic tree analysis, we propose that bacterial cellobiohydrolases are designed to degrade crystalline cellulose using high-affinity CBD and high-processivity CD.

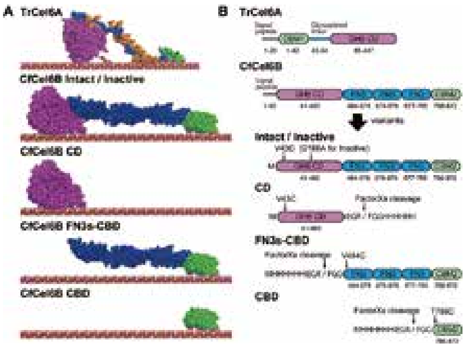

Figure 2. Structures of TrCel6 and CfCel6B. A, model structures of Intact TrCel6A, CfCel6B, and CfCel6B domain constructs used in this study. TrCel6A structure is the same as in the previous report. For CfCel6B, structure of CD is X-ray crystal structure (PDB code 7CBD), and FN3s and CBD are modeled by SWISS-MODEL server. Figures were prepared by PyMOL. B, detailed descriptions of domain compositions for each construct. Positions of mutation sites, histidine tags, and FaXa cleavage sites and estimated amino acid numbers for each domain are shown.

2. Combined Approach to Engineer a Highly Active Mutant of Processive Chitinase Hydrolyzing Crystalline Chitin[2)]

Serratia marcescens chitinase A (SmChiA) processively hydrolyzes recalcitrant biomass crystalline chitin under mild conditions. Here, we combined multiple sequence alignment, site-saturation mutagenesis, and automated protein purification and activity measurement with liquid-handling robot to reduce the number of mutation trials and shorten the screening time for hydrolytic activity improvement of SmChiA. The amino acid residues, which are not conserved in the alignment and are close to the aromatic residues along the substrate-binding sites in the crystal structure, were selected for site-saturation mutagenesis. Using the previously identified highly active F232W/F396W mutant as a template, we identified the F232W/F396W/S538V mutant, which shows further improved hydrolytic activity just by trying eight different sites. Importantly, valine was not found in the multiple sequence alignment at Ser538 site of SmChiA. Our combined approach allows engineering of highly active enzyme mutants, which cannot be identified only by the introduction of predominant amino acid residues in the multiple sequence alignment.

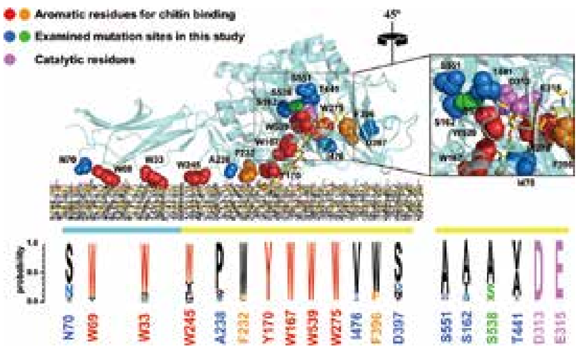

Figure 3. Model structure of SmChiA bound to crystalline chitin, important residues for binding and catalysis, and residues mutated in this study. (Top) A crystal structure of SmChiA (PDB entry 1CTN; ribbon model) aligned with the crystalline chitin chains (stick model). Amino acid residues responsible for binding to chitin (red and orange), catalytic residues (pink), and examined mutation sites (blue and green) are highlighted with sphere models. An expanded image around the catalytic site (transparent box in the left structure) is also shown in the right-hand-side box with 45° turn from the left structure. The cyan and yellow bars under the structure indicate the binding and catalytic domains, respectively. (Bottom) Result of multiple sequence alignment for amino acid residues highlighted in the top. The residues of SmChiA are shown in the same color as the top.

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2) A, Visootsat *et al.*, *ACS Omega* **5**, 26807–26816 (2020).

Award

OTOMO, Akihiro; Best Presentation Award, 2020 Annual Meeting of the Biophysical Society of Japan Chubu Branch Meeting (2020).

Development of Heterogeneous Catalysis toward Ideal Chemical Processes

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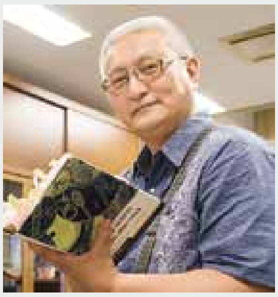

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1995 Lecturer, Kyoto University
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Professor, The Graduate University for Advanced Studies
2007 Research team leader, RIKEN
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2003 Research Project Leader, JST CREST Project (−2008)
2008 Research Project Leader, NEDO Project (−2012)
2011 Deputy Research Project Leader, JST CREST (−2016)
2014 Research Project Leader, JST ACCEL Project (−2019)

Awards
1991 Eisai Award, Synthetic Organic Chemistry
1998 The Pharmaceutical Society of Japan Award for Young Scientist
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TAKAHASHI, Teruki
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TAZAWA, Aya
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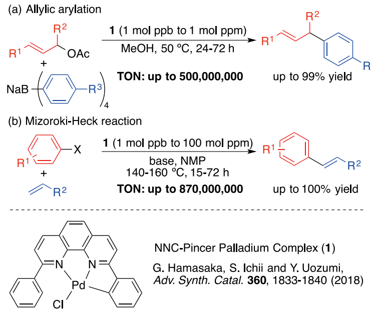
TANIWAKE, Mayuko

Keywords Transition Metal Catalysis, Green Chemistry, Organic Synthesis

Our research interests lie in the development of transition metal-catalyzed reaction systems toward ideal (highly efficient, selective, green, safe, simple, etc.) organic transformations. In particular, we have recently been developing the heterogeneous aquacatalytic systems, continuous flow catalytic systems, and super active catalysts working at ppm-ppb loading levels. Thus, for example, a variety of palladium catalysts were designed and prepared promoting carbon–carbon bond forming reactions at ppm-ppb loading levels (Figure 1).



NNC-Pincer Palladium Complex (**1**)
G. Hamasaka, S. Ichii and Y. Uozumi, *Adv. Synth. Catal.* **360**, 1833-1840 (2018)

Figure 1. Typical Examples of Pd-Catalyzed Carbon–Carbon Bond Forming Reactions with ppm-ppb Loading Levels of an NNC-Pincer Pd Complexes.

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1. C–H Arylation of Thiophenes with Aryl Bromides by a Parts-per-Million Loading of a Palladium NNC-Pincer Complex[1]

A palladium NNC-pincer complex efficiently catalyzed the direct arylation of thiophene derivatives with extremely low palladium loadings of the order of parts per million. Thus, the reaction of various thiophenes with aryl bromides in the presence of 25–100 mol ppm of chlorido[(2-phenyl-κ-C ^{2})-9-phenyl-1,10-phenanthroline-κ^2-*N*,*N*′]palladium(II) NNC-pincer complex, K_2CO_3, and pivalic acid in *N*,*N*-dimethylacetamide afforded the corresponding 2- or 5-arylated thiophenes in good to excellent yields. A combination of the present C–H arylation and Hiyama coupling with the same NNC-pincer complex provides an efficient synthesis of unsymmetrical 2,5-thiophenes with catalyst loadings at mol ppm levels.

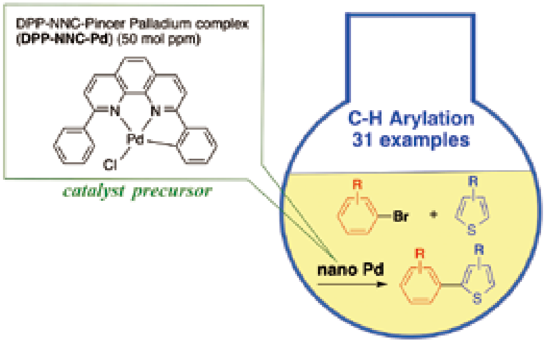

Figure 2. C−H Arylation of Thiophenes with Aryl Bromides by a Parts-per-Million Loading of a Palladium NNC-Pincer Complex.

2. A Convoluted Polyvinylpyridine-Palladium Catalyst for Suzuki-Miyaura Coupling and C–H Arylation[2]

The development of highly active and reusable supported catalysts for Suzuki-Miyaura coupling and catalytic C–H arylation is important for fundamental and applied chemistry, with these reactions being used to produce medical compounds and functional materials. We found that a mesoporous composite made of a linear poly(4-vinylpyridine) and tetrachloropalladate acted as a dual-mode catalyst for a variety of cross-coupling reactions, with both Pd nanoparticles and a Pd complex catalyst being observed under different conditions. The polyvinylpyridine-palladium composite was readily prepared via the molecular convolution of poly(4-vinylpyridine) and sodium tetrachloropalladate to provide a hardly soluble polymer-metal composite. The Suzuki-Miyaura coupling and the C–H arylation of aryl chlorides and bromides with arylboronic acids, thiophenes, furans, benzene, and anisole proceeded in the presence of 0.004 mol% (40 mol ppm) to 1 mol% Pd to afford the corresponding coupling products in high yields. Furthermore, the catalyst was reused without an appreciable loss of activity. Pharmaceutical compounds and functional materials were synthesized via the coupling reactions. N_2 gas adsorption/desorption analysis indicated that the catalyst had a mesoporous nature, which played a crucial role in the catalysis. In the Suzuki-Miyaura couplings, in situ generated palladium nanoparticles in the polymer matrix were catalytically active, while a polymeric Pd(II) complex was crucial in the C–H arylations. These catalytic species were investigated via XAFS, XPS, far-infrared absorption, and Raman spectroscopies, as well as DFT calculations.

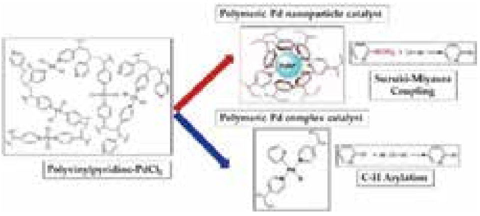

Figure 3. Polyvinylpyridine-Palladium Catalyst for Suzuki-Miyaura Coupling and C−H Arylation.

3. Synthesis of α-Tertiary Amines by the Ruthenium-Catalyzed Regioselective Allylic Amination of Tertiary Allylic Esters[3]

We demonstrated a ruthenium-catalyzed regioselective allylic amination of tertiary allylic esters with various amines using $[Cp^*Ru(CH_3CN)_3][PF_6]$/5,5′-dimethyl-2,2′-bipyridine (5,5′-diMe-2,2′-bpy) and related ruthenium catalytic systems, and successfully obtained a diverse range of α-tertiary amines as single regioisomers. The present ruthenium catalytic system was effective for reactions with various types of amines.

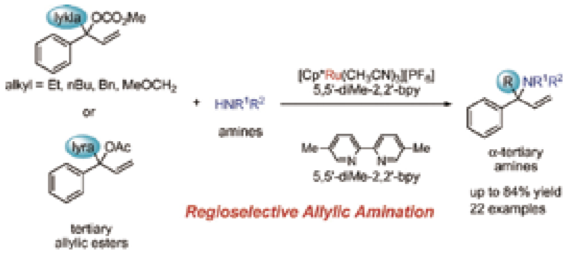

Figure 4. Ruthenium-catalyzed Regioselective Allylic Amination of Tertiary Allylic Esters.

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3) S. Ichii, G. Hamasaka and Y. Uozumi, *Chem. Lett.* **49**, 645–647 (2020).

Design and Synthesis of Chiral Organic Molecules for Asymmetric Synthesis

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Keywords Synthetic Chemistry, Molecular Catalyst, Non-Covalent Interaction

The field of molecular catalysis has been an attractive area of research to realize efficient and new transformations in the synthesis of functional molecules. The design of ligands and chiral molecular catalysts has been recognized as one of the most valuable strategies; therefore, a great deal of effort has been dedicated to the developments. In general, "metal" has been frequently used as the activation center, and conformationally rigid catalyst framework has been preferably components for the catalyst design. To develop new type of molecular catalysis, we have focused on the use of hydrogen and halogen atom as activation unit, and have utilized non-covalent interactions as organizing forces of catalyst framework in the molecular design of catalyst, which had not received much attention until recently. We hope that our approach will open the new frontier in chiral organic molecules from chiral molecular chemistry to chiral molecular science.

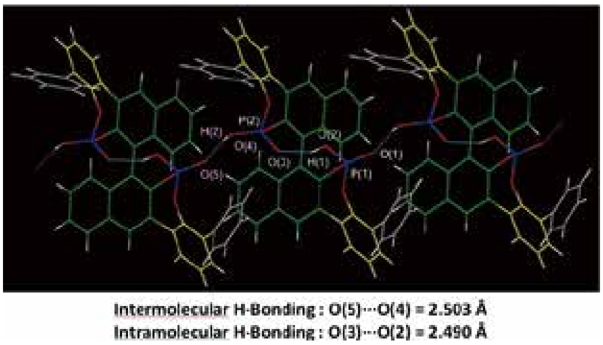

Figure 1. Hydrogen bonding network in chiral bis-phosphoric acid catalyst derived from (*R*)-3,3'-di(2-hydroxy-3 -arylphenyl)binaphthol. Hydrogen bond acts as activation unit for the substrate in asymmetric reaction space and controls atropisomeric behavior in naphthyl–phenyl axis.

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- N. Momiyama, T. Konno, Y. Furiya, T. Iwamoto and M. Terada, "Design of Chiral Bis-Phosphoric Acid Catalyst Derived from (*R*)-3,3'-Di(2-hydroxy-3-arylphenyl)binaphthol: Catalytic Enantioselective Diels–Alder Reaction of α,β-Unsaturated Aldehydes with Amidodienes," *J. Am. Chem. Soc.* **133**, 19294–19297 (2011).
- N. Momiyama, H. Tabuse, H. Noda, M. Yamanaka, T. Fujinami, K. Yamanishi, A. Izumiseki, K. Funayama, F. Egawa, S. Okada, H. Adachi and M. Terada, "Molecular Design of a Chiral Brønsted Acid with Two Different Acidic Sites: Regio-, Diastereo-, and Enantioselective Hetero-Diels–Alder Reaction of Azopyridinecarboxylate with Amidodienes Catalyzed by Chiral Carboxylic Acid–Monophosphoric Acid," *J. Am. Chem. Soc.* **138**, 11353–11359 (2016).

1. Brønsted Acid Catalyzed Asymmetric Rearrangement: Asymmetric Synthesis of Linear Homoallylic Amines

Allylation of imines with allylic metal reagents has been one of the most valuable tools to synthesize enantioenriched homoallylic amines. Due to the inherent nature of allylic metal reagent, however, regioselectivity has been a long-standing subject in this area. To develop the synthetic reaction for enantioenriched linear homoallylic amines, we discovered chirality transferred formal 1,3-rearrangement of ene-aldimines in the presence of Brønsted acid, and developed it as synthetic method for variety of enantioenriched linear homoallylic amines.1) Furthermore, we studied details of reaction mechanism and succeeded catalytic asymmetric version of this rearrangement.2) On the basis of this study, catalytic asymmetric version of this reaction was developed.3) To the best our knowledge, our discovery is the first example of catalytic asymmetric methylene migration.

2. Design of Chiral Brønsted Acid Catalyst

Chiral Brønsted acid catalysis has been recognized as one of the useful tools in asymmetric synthesis. We have contributed to this area by focusing on the use of perfluoroaryls and C_1-symmetric design.

Perfluorinated aryls have emerged as an exquisite class of motifs in the design of molecular catalysts, and their electronic and steric alterations lead to notable changes in the chemical yields and the stereoselectivities. We developed the perfluoaryls-incorporated chiral mono-phosphoric acids as chiral Brønsted acid catalysts that can deriver high yields and stereoselectivities in the reactions of imines with unactivated alkenes. We have described the first example of a diastereo- and enantioselective [4+2] cycloaddition reaction of *N*-benzoyl imines, as well as the enantioselective three-component imino–ene reaction using aldehydes and $\mathrm{FmocNH_2}$.4)

We have developed (*R*)-3,3'-di(2-hydroxy- 3-arylphenyl) binaphthol derived chiral bis-phosphoric acid which efficiently catalyzed enantioselective Diels–Alder reaction of acroleins with amidodienes.5,6) We demonstrated that two phosphoric acid groups with individually different acidities can play distinct roles in catalyst behavior through hydrogen bonding interactions. Therefore, we developed a Brønsted acid with two different acidic sites, aryl phosphinic acid-phosphoric acid.7) Furthermore, molecular design of a chiral Brønsted acid with two different acidic sites, chiral carboxylic acid–cyclic mono-phosphoric acid, was identified as a new and effective concept in asymmetric hetero-Diels–Alder reaction of 2-azopyridinoester with amidodienes.8)

3. Design of Catalysis with Halogen Bond for Carbon–Carbon Bond Forming Reactions

Halogen bonds are attractive non-covalent interactions between terminal halogen atoms in compounds of the type R—X (X = Cl, Br, I) and Lewis bases LBs. It has been known that strong halogen bonds are realized when "R" is highly electronegative substituents such as perfluorinated alkyl or aryl substituents. We recently developed synthetic methodology for perfluorinated aryl compounds and applied it for the development of chiral Brønsted acid catalysts. On the basis of our achievements, we have examined it to develop catalysis with halogen bond for carbon–carbon bond forming reactions.9)

We found that perfluorinated iodoaryls are able to catalyze the allylation reaction to *N*-activated heteroaromatics. On the basis of this discovery, a quantitative approach was studied using 4-substituted perfluorinated iodobenzene.10) Examination of the electrostatic potential surfaces showed that substituent R groups significantly affected the charge density of iodine, fluorine, and carbon on the benzene ring. ^{19}F NMR titrations were used to determine the binding constants K for chloride, and their catalytic activities were evaluated in the allylation reaction. We revealed that the log K and product yields were linearly correlated, and that they were dependent on the Hammett substituent parameter, σ_{meta}. This linear correlation provided a quantitative predictive model for both the binding constant and the reaction yield. Concomitantly, this efficiently permitted the development of a highly active anion-binding catalyst, namely $\mathrm{4\text{-}CNC_6F_4I}$. The catalytic activity of $\mathrm{4\text{-}CNC_6F_4I}$ was established in the allylation and crotylation of silatrane reagents to *N*-activated isoquinolines.

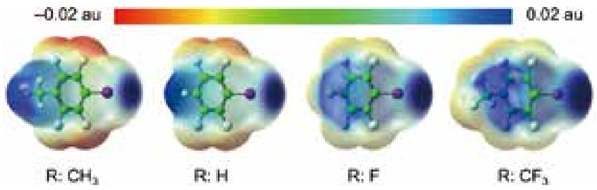

Figure 2. Molecular electrostatic potential surfaces of $\mathrm{4\text{-}RC_6F_4I}$ (R: $\mathrm{CH_3}$, H, F, and $\mathrm{CF_3}$) at the M06-2X-D3/6-311+G(d,p)-SDD level of theory.

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Creation of Novel Photonic-Electronic-Magnetic Functions Based on Molecules with Open-Shell Electronic Structures

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Keywords Radical, Open-Shell Electronic States, Photonic-Electronic-Magnetic Properties

The molecules with open-shell electronic states can exhibit unique properties, which are difficult to achieve for conventional closed-shell molecules. Our group develops new open-shell organic molecules (= radicals) and metal complexes to create novel photonic-electronic-magnetic functions.

While conventional closed-shell luminescent molecules have been extensively studied as promising components for organic light-emitting devices, the luminescent properties of radicals have been much less studied because of its rarity and low chemical (photo-)stability. We have developed highly photostable luminescent organic radicals, PyBTM and its analogues, and investigated photofunctions attributed to their open-shell electronic states. We have discovered that (i) PyBTM-doped molecular crystals exhibit photoluminescence at RT with $\varphi_{\mathrm{em}} = 89\%$, which is exceptionally high in radicals, (ii) radical-doped crystals and radical-based coordination polymers exhibit drastic changes in the emission spectra by applying a magnetic field. These are the first demonstrations of magnetoluminescence in radicals, and are attributed to interplay between the spin and the luminescence. Our studies provide novel and unique concepts in molecular photonics, electronics, and spintronics, and also bring innovative ideas in the development of light-emitting devices.

Our group focuses on strongly-interacted spins in molecular crystals. The anisotropic assembly of open-shell molecules in crystalline states enables unique molecular materials with exotic electrical and magnetic properties, such as superconductors, ferromagnets, and quantum spin liquids.

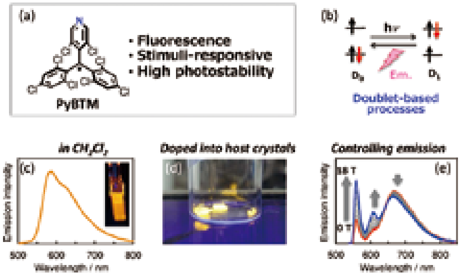

Figure 1. (a) Molecular structure of PyBTM and its characteristics. (b) Schematic photoexcitation-emission processes. (c) Emission in CH_2Cl_2. (d) Emission of PyBTM-doped molecular crystals. (e) Controlling emission by magnetic field.

Selected Publications

- S. Kimura, M. Uejima, W. Ota, T. Sato, S. Kusaka, R. Matsuda, H. Nishihara and T. Kusamoto, "An Open-Shell, Luminescent, Two-Dimensional Coordination Polymer with a Honeycomb Lattice and Triangular Organic Radical," *J. Am. Chem. Soc.* **143**, 4329–4338 (2021).
- S. Kimura, T. Kusamoto, S. Kimura, K. Kato, Y. Teki and H. Nishihara, "Magnetoluminescence in a Photostable, Brightly Luminescent Organic Radical in a Rigid Environment," *Angew. Chem., Int. Ed.* **57**, 12711–12715 (2018).
- Y. Hattori, T. Kusamoto and H. Nishihara, "Enhanced Luminescent Properties of an Open-Shell (3,5-Dichloro-4-pyridyl)bis(2,4,6-trichlorophenyl)methyl Radical by Coordination to Gold," *Angew. Chem., Int. Ed.* **54**, 3731–3734 (2015).
- Y. Hattori, T. Kusamoto and H. Nishihara, "Luminescence, Stability, and Proton Response of an Open-Shell (3,5-Dichloro-4-pyridyl)bis(2,4,6-trichlorophenyl)methyl Radical," *Angew. Chem., Int. Ed.* **53**, 11845–11848 (2014).

1. An Open-Shell, Luminescent, Two-Dimensional Coordination Polymer with a Honeycomb Lattice Based on Triangular Radical

Two-dimensional (2D) open-shell coordination polymers (CPs) with honeycomb lattices have attracted growing interest because of the exotic electronic structures and physical properties derived from their structural topology. Employing organic radicals as building blocks is a promising approach to produce open-shell CPs. However, radical-based CPs with honeycomb lattices reported generally have low chemical stability or poor crystallinity. Accordingly, high crystallinity and persistence are in strong demand in this class of compounds. In this study, we developed a novel triangular organic radical tris(3,5-dichloro-4-pyridyl)methyl radical (trisPyM) possessing three pyridyl groups.[1] trisPyM demonstrates photoluminescence (λ_{em} = 700 nm, φ_{em} = 0.85%, τ = 3.0 ns in dichloromethane) and high photostability with its half-life upon UV irradiation 10000 times that of TTM, a conventional luminescent radical. Complexation of trisPyM with $\mathrm{Zn^{II}(hfac)_2}$ afforded single crystals of a novel 2D CP, trisZn, possessing a honeycomb lattice with graphene-like spin topology (Figure 2). The coordination structure of trisZn is stable under evacuation at 60 °C. trisZn exhibits photoluminescence below 79 K at λ_{em} = 695 nm. Importantly, trisZn displays magnetoluminescence below 20 K.[2] This is the first example showing magnetoluminescence as pure (*i.e.*, non-doped) radical compounds. Our results indicate that trisPyM can be a promising building block in the construction of a new class of 2D honeycomb CPs with spin-correlated novel photofunctions.

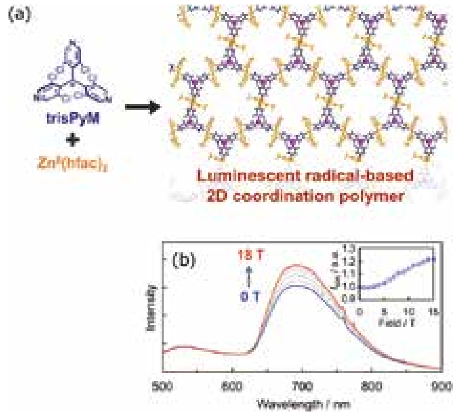

Figure 2. (a) Chemical structure of trisPyM and crystal structure of trisZn. (b) Emission spectra of trisZn at 4.2 K under a magnetic field.

2. Solid-State Room-Temperature Near-Infrared Photoluminescence of a Stable Organic Radical

Luminescent organic radicals have been shown to demonstrate unique emission properties in solvents or in host materials. On the other hand, the luminescent properties of radicals in the fully aggregated pure solid state have rarely been investigated, especially at room temperature. In this study, a novel luminescent radical with a 3-pyridyl moiety, the (2,4-dichloro-3-pyridyl)bis(2,4,6-trichlorophenyl)methyl radical (metaPyBTM) was prepared and the optical properties were investigated in detail.[3] metaPyBTM exhibits distinct near-infrared photoluminescence in its crystalline state at room temperature, in spite of the fact that the electronic structure and photophysical properties in solution are similar to those of the analogues radicals. The solid-state luminescence properties of metaPyBTM are modulated strongly by temperature and the degree of aggregation. metaPyBTM in the moderately aggregated state displays magnetic-field responsive luminescence, magnetoluminescence, whereas no magnetic field effect was detected in the emission spectrum of purely crystalline metaPyBTM. These results suggest that controlling the manner of interactions between radicals is an important factor for achieving magnetoluminescence.

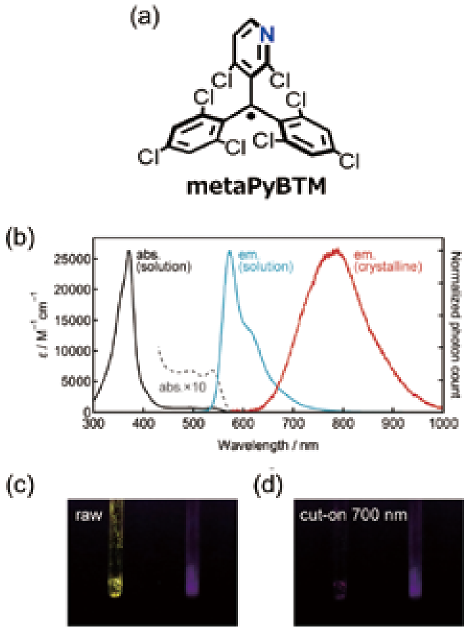

Figure 3. (a) Chemical structure of metaPyBTM. (b) Absorption and emission spectra of metaPyBTM in dichloromethane (black, pale-blue) and in crystalline state (red). (c,d) Vis-NIR photographs of pure metaPyBTM (right) and metaPyBTM-doped αH-metaPyBTM crystals under UV light at λ = 365 nm with (d) and without (c) a longpass filter (cut-on: 700 nm). Photos were taken by BIZWORKS Yubaflex digital camera.

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Design and Synthesis of Three-Dimensional Organic Structures

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2005	B.S. The University of Tokyo
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Professional Employment

2009	Assistant Professor, Nagoya University
2013	Designated Associate Professor, Nagoya University
2013	Group Leader and Project Coordinator, JST ERATO Itami Molecular Nanocarbon Project (until 2020)
2020	Associate Professor, Institute for Molecular Science Associate Professor, The Graduate University for Advanced Studies

Award

2013	RSC PCCP Prize
2014	Akasaki Award
2017	Chemical Society of Japan Award for Young Chemists
2018	The Commendation for Science and Technology by the Minister of Education, Culture, Sports, Science and Technology The Young Scientists' Prize
2019	Nozoe Memorial Award for Young Organic Chemists

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Keywords π-Conjugated Molecules, Molecular Topology, 3D Network Polymer

Aromatic compounds are potentially useful as functional electronic materials. However, the controlled synthesis and assembly of three-dimensional complex molecules are still very difficult, especially for the crystal engineering of organic molecules. This group aims to create novel topological and reticular organic structures by using synthetic organic chemistry and geometric insights.

To achieve our purpose, this group will start electron-diffraction crystallography (MicroED) for the rapid structure determination of organic compounds. While X-ray crystallography is a general and reliable method for structure determination, it requires ~0.1 mm single crystals and making such crystal sometimes needs tremendous times and efforts. Since electron beam have much higher diffraction intensity than X-ray, structural analysis can be performed even with ultra-small crystals (1 µm or less). There are many fields such as covalent organic crystals with a three-dimensional structure and molecules with complex molecular topologies, where structural analysis has not been sufficiently developed.

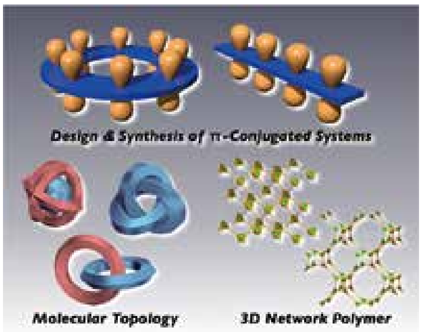

Figure 1. Design and synthesis of π-conjugated organic molecules (top); Development of novel molecular topology (bottom left); Construction of three-dimensional network polymers (bottom right).

Selected Publications

- K. Kato, K. Takaba, S. Maki-Yonekura, N. Mitoma, Y. Nakanishi, T. Nishihara, T. Hatakeyama, T. Kawada, Y. Hijikata, J. Pirillo, L. T. Scott, K. Yonekura, Y. Segawa and K. Itami, "Double-Helix Supramolecular Nanofibers Assembled from Negatively Curved Nanographenes," *J. Am. Chem. Soc.* **143**, 5465–5469 (2021).
- K. Y. Cheung, K. Watanabe, Y. Segawa and K. Itami, "Synthesis of a Zigzag Carbon Nanobelt," *Nat. Chem.* **13**, 255–259 (2021).
- Y. Saito, K. Yamanoue, Y. Segawa and K. Itami, "Selective Transformation of Strychnine and 1,2-Disubstituted Benzenes by C–H Borylation," *Chem* **6**, 985–993 (2020).
- Y. Segawa, D. R. Levine and K. Itami, "Topologically Unique Molecular Nanocarbons," *Acc. Chem. Res.* **52**, 2760–2767 (2019).
- Y. Segawa, M. Kuwayama, Y. Hijikata, M. Fushimi, T. Nishihara, J. Pirillo, J. Shirasaki, N. Kubota and K. Itami, "Topological Molecular Nanocarbons: All-Benzene Catenane and Trefoil Knot," *Science* **365**, 272–276 (2019).
- G. Povie, Y. Segawa, T. Nishihara, Y. Miyauchi and K. Itami, "Synthesis of a Carbon Nanobelt," *Science* **356**, 172–175 (2017).
- Y. Segawa and D. W. Stephan, "Metal-Free Hydrogenation Catalysis of Polycyclic Aromatic Hydrocarbons," *Chem. Commun.* **48**, 11963–11965 (2012).

1. Double-Helix Supramolecular Nanofibers Assembled from Negatively Curved Nanographenes

The layered structures of graphite and related nanographene molecules play a key role in their physical and electronic properties. The well-ordered molecular alignment of nanographenes and its structural determination are of interest in order to gain insight into a variety of carbon materials. It is well known that the one-dimensional (1D) assembly of planar nanographenes can be achieved by introducing suitable peripheral substituents that tune solubility. The 1D assembly of bowl-shaped nanographenes was also achieved by convex-concave π-π stacking along with non-covalent interactions. However, the stacking modes of negatively curved nanographenes remain unclear, owing to the lack of suitable nanographene molecules.

We developed the synthesis and 1D self-assembly of a newly designed nanographene **1-H** ($C_{68}H_{28}$), a negatively curved nanographene with 12 carbon atoms fewer than WNG (Figure 2a).1) Serendipitously, we discovered that **1-H** self-assembles in various organic solvents and works as a highly efficient gelator that forms organic gels at concentrations of <1 wt% (Figure 2b). Transmission electron microscopy (TEM) and atomic force microscopy (AFM) measurements confirm that **1-H** forms fibers with diameters of ~2.8 nm. The presence of efficient π-π interactions in the fiber structures is supported by a bathochromic shift in the fluorescence spectrum of the gel state relative to that of dilute solutions of **1-H**. Finally, using three-dimensional electron diffraction crystallography, the double-helix π-π stacking mode of **1-H** in the supramolecular nanofiber was revealed (Figure 2c).

Based on this discovery and its revelation of a new guiding principle in supramolecular self-assembly, we expect that a number of negatively curved nanographenes can be developed for new applications in materials science and biology. Moreover, this work not only reports the discovery of an all-sp^2-carbon supramolecular π-organogelator with negative curvature, but it also showcases the power of 3D electron diffraction crystallography for the structural determination of submicrometer-sized hydrocarbon molecular assemblies.

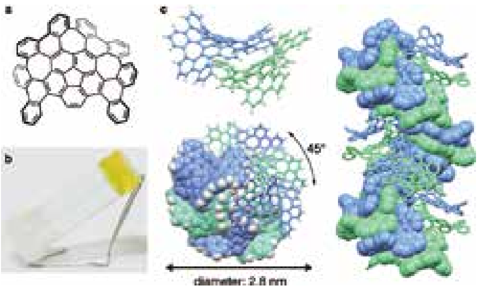

Figure 2. The negatively curved nanographene (**1-H**) that forms double-helix nanofibers. (a) Chemical structure of **1-H**. (b) Photo of organogel made of dichloromethane with 0.3 wt% of **1-H**. (c) The double-helix packing structure of **1-H** revealed by microcrystal electron diffraction crystallography (MicroED).

2. Theoretical Studies on the Strain Energy of Helicene-Containing Carbon Nanobelts

Carbon nanobelts (CNBs), the sidewall segment molecules of carbon nanotubes (CNTs), have attracted growing attention owing to their radial π-conjugation, strain-induced reactivity and potential applications in template CNT synthesis. Various CNB structures have been proposed and investigated by both theoretical and synthetic organic chemists. Recently, our group synthesized armchair-type (*n*,*n*)CNB (**A*n***, Figure 3a) and a zigzag-type (18,0)CNB. Apart from these known CNBs, other CNBs with more complex structures can also be designed by cutting the CNTs differently. CNBs with helicene structures (**B*n***–**E*n***, Figure 3b) are the representative examples of these complex structures, and the structural properties of such unexplored CNBs have been of interest.

To estimate the feasibility of synthesizing strained belt-shaped compounds, the calculation of strain energy (SE) is effective. While homodesmotic reaction method using reference molecules is generally used for strained molecules, we previously found that conventional homodesmotic reactions using small reference molecules could not be applied to CNBs.

Here we have successfully estimated the strain energies of CNBs containing helicene moieties.2) Through the calculation of CNB **B*n***, we revealed that our previously reported method is not applicable to helicene-containing CNBs. The newly developed method, combining the conventional homodesmotic reactions and linear regression analysis, was successful for the determination of the strain energies of CNBs **B*n*** and **C*n*** that have helicene moieties in their side chains. By changing the reference molecules, the strain energies of CNBs with helicene structures in the main chains (**D*n*** and **E*n***) were also determined.

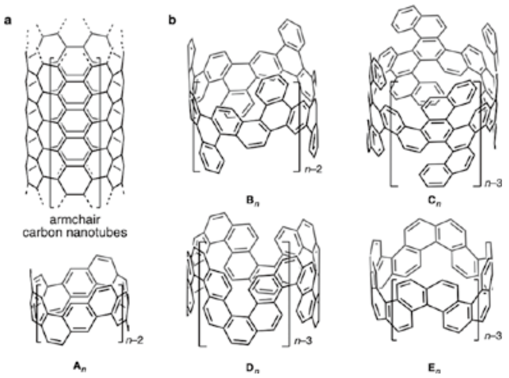

Figure 3. (a) Structures of armchair CNTs and CNBs (**A*n***). (b) CNBs containing helicene structures (**B*n***–**E*n***).

References

1) K. Kato, K. Takaba, S. Maki-Yonekura, N. Mitoma, Y. Nakanishi, T. Nishihara, T. Hatakeyama, T. Kawada, Y. Hijikata, J. Pirillo, L. T. Scott, K. Yonekura, Y. Segawa and K. Itami, *J. Am. Chem. Soc.* **143**, 5465–5469 (2021).

2) K. Watanabe, Y. Segawa and K. Itami, *Chem. Commun.* **56**, 15044–15047 (2020).

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Visiting Professors

Visiting Professor

FUKAZAWA, Aiko *(from Kyoto University)*

Renaissance of Nonbenzenoid π-Conjugated Systems toward Functional Materials

The work of our group has focused on exploring functional organic compounds with unusual with superb optical and/or electronic properties, based on the molecular designs of novel π-conjugated scaffolds as well as unusual functional groups. In particular, we have recently proposed a rational design of stable yet unusual π-conjugated systems based on the characteristics of nonbenzenoid hydrocarbons, *i.e.*, dehydroannulenes, non-alternant hydrocarbons, and fulvalenes, by annulation of weakly aromatic (hetero)arenes. In this year, we have succeeded in synthesizing several thiophene-fused antiaromatic π-systems that exhibit high thermal stability even without bearing bulky substituents while retaining pronounced antiaromatic character. Moreover, we have recently succeeded in synthesizing the fulvalene-based π-conjugated oligomers that exhibit exceptional electron-accepting character as well as the robustness toward multi-electron reduction.

Visiting Professor

WATANABE, Rikiya *(from RIKEN)*

Single Molecule Physiology

Our study aims to understand cellular functions using a bottom-up approach from the single molecule level. To achieve this, we are attempting to elucidate the mechanism by which individual biomolecules or their networks function in a precise manner, by developing novel single-molecule techniques using multidisciplinary approaches, including biophysics, bioMEMS, and chemical biology. In addition, we are developing a methodology to investigate correlations between genetic mutations, dysfunctions, and diseases with single molecule sensitivity, which would provide new insights for biological as well as pharmaceutical studies. Notably, last year, we developed a novel technology that can identify new coronavirus, SARS-CoV-2, at the single molecule level, enabling the world's fastest quantitative detection for early diagnosis.

Visiting Associate Professor

UEDA, Akira *(from Kumamoto University)*

Development of Purely Organic Molecular Materials with Three-Dimensional Electronic Structure

Design and synthesis of novel molecular materials have been a central issue for the development of molecular science. Our group has recently succeeded in the development of a new type of molecular conductor crystal composed of a zwitterionic neutral radical with a partially charge-transferred structure. Single crystal X-ray analysis reveals that this material has a peculiar electronic structure where two-dimensional conducting layers are electronically coupled to each other through the intramolecular interaction of the partially charge-transferred zwitterionic neutral radical. Therefore, one can say that this material has a three-dimensional-like electronic structure different from one- or two-dimensional ones in the conventional molecular conductors. Interestingly, the low-temperature structural analysis and physical property measurements suggest that this material undergoes a phase transition from the charge-uniform state to a three-dimensionally charge-ordered state.

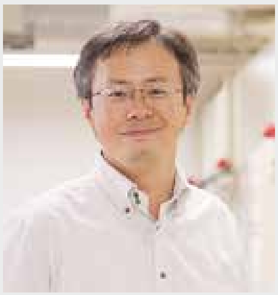
RESEARCH ACTIVITIES

Research Center of Integrative Molecular Systems

The mission of CIMoS is to analyze molecular systems in nature to find the logic behind the sharing and control of information between the different spatiotemporal hierarchies, with the ultimate goal of creating novel molecular systems on the basis of these findings.

Biological Rhythm and Dynamics through Chemistry

Research Center of Integrative Molecular Systems
Division of Trans-Hierarchical Molecular Systems



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2005	JST-PRESTO Researcher
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2012	Professor, Institute for Molecular Science Professor, The Graduate University for Advanced Studies

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2007	Young Scientist Prize, The Biophysical Society of Japan
2006	SAS Young Scientist Prize, IUCr Commission on Small-angle Scattering
2002	The Protein Society Annual Poster Board Award

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SUZUKI, Hiroko

Keywords Biological Rhythm, Circadian Clock, Cyanobacteria

Living organisms on Earth evolved over time to adapt to daily environmental alterations, and eventually acquired endogenous time-measuring (biological clock) systems. Various daily activities that we perform subconsciously are controlled by the biological clock systems sharing three characteristics. First, the autonomic rhythm repeats with an approximately 24-hour (circadian) cycle (self-sustainment). Second, the period is unaffected by temperature (temperature compensation). Third, the phase of the clock is synchronized with that of the outer world in response to external stimuli (synchronization). We seek to explain these three characteristics, and consider the biological clock system of cyanobacteria to be an ideal experimental model.

The major reason that cyanobacteria are considered to be the ideal experimental model is that the core oscillator that possesses the three characteristics of the clock can be easily reconstructed within a test tube. When mixing the three clock proteins KaiA, KaiB, and KaiC with ATP, the structure and enzyme activity of KaiC change rhythmically during a circadian cycle. Taking advantage of this test tube experiment, we used an approach combining biology, chemistry, and physics to elucidate the means by which the clock system extends from the cellular to atomic levels.

Among the three Kai proteins, KaiC is the core protein of the oscillator. In the presence of KaiA and KaiB, KaiC revelas the rhythm of autophosphorylation and dephosphorylation; however, the cycle of this rhythm depends on the ATPase activity of KaiC independent of KaiA or KaiB. For example, when the ATPase activity of KaiC doubles as a result of amino acid mutations, the frequencies of both the *in vitro* oscillator and the intracellular rhythm also double (the cycle period is reduced to half). This mysterious characteristic is called a transmural hierarchy, in which the cycle (frequency) and even the temperature compensation both *in vitro* and *in vivo* are greatly affected (controlled) by the function and structure of KaiC.

How are the circadian activities and temperature compensation features encoded in KaiC and then decoded from it to propagate rhythms at the cellular level? We are committed to better understanding biological clocks and other dynamic systems through the chemistry of circadian ***rhythm***, ***structure***, and evolutionary ***diversity***.

Selected Publications

- D. Ouyang, Y. Furuike, A. Mukaiyama, K. Ito-Miwa, T. Kondo and S. Akiyama, *Int. J. Mol. Sci.* **20**, 2789–2800 (2019).
- A. Mukaiyama, D. Ouyang, Y. Furuike and S. Akiyama, *Int. J. Biol. Macromol.* **131**, 67–73 (2019).
- A. Mukaiyama, Y. Furuike, J. Abe, E. Yamashita, T. Kondo and S. Akiyama, *Sci. Rep.* **8**, 8803 (2018).
- J. Abe, T. B. Hiyama, A. Mukaiyama, S. Son, T. Mori, S. Saito, M. Osako, J. Wolanin, E. Yamashita, T. Kondo and S. Akiyama, *Science* **349**, 312–316 (2015).
- Y. Murayama, A. Mukaiyama, K. Imai, Y. Onoue, A. Tsunoda, A. Nohara, T. Ishida, Y. Maéda, T. Kondo and S. Akiyama, *EMBO J.* **30**, 68–78 (2011).
- S. Akiyama, A. Nohara, K. Ito and Y. Maéda, *Mol. Cell* **29**, 703–716 (2008).

1. *Structure*: Reasons for Seeking Structure and Dynamics of Circadian Clock Components in Cyanobacteria1–3)

A great deal of effort has been devoted to characterizing structural changes in the clock proteins along the circadian reaction coordinate.1) However, little is known about the mechanism driving the circadian cycle, even for the simple cyanobacterial protein KaiC that has ATPase and dual phosphorylation sites in its N-terminal C1 and C-terminal C2 domains, respectively. Nearly all KaiC structures reported to date share a nearly identical structure, and they do not appear to be suggestive enough to explain the determinants of circadian period length and its temperature compensation. We are studying the structural and dynamical origins in KaiC using high-resolution x-ray crystallography2) and quasielastic neutron scattering,3) respectively.

2. *Rhythm*: Cross-Scale Analysis of Cyanobacterial Circadian Clock System3–5)

KaiC ATPase is of particular interest here, as it finely correlates to the frequencies of *in vivo* as well as *in vitro* oscillations and also it is temperature compensated. This unique property has inspired us to develop an ATPase-based screening for KaiC clock mutants4) giving short, long, and/or temperature-dependent periods. A developed HPLC system with a 4-channel temperature controller has reduced approximately 80% of time costs for the overall screening process (Figure 1). Using the developed device, we are screening a number of temperature-dependent mutants of KaiC.3)

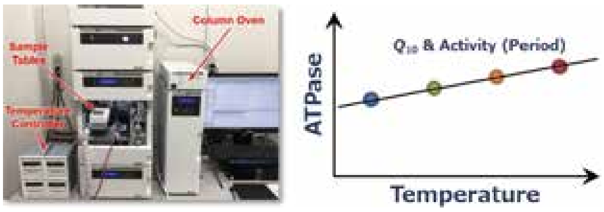

Figure 1. Development of a quick ATPase assay system.

We also collaborated with Drs. Ito-Miwa and Kondo (Nagoya University) to identify a series of KaiC mutations altering circadian periods dramatically, from 0.6 to 6.6 d.5)

3. beyond Evolutionary *Diversity*6)

In the presence of KaiA and KaiB, the ATPase activity of KaiC oscillates on a 24-hour cycle. KaiC is not capable of maintaining a stable rhythm on its own, but its activity was observed to fluctuate with reduced amplitude over time (Figure 2A). We have identified a signal component that is similar to damped oscillation, and propose that it encodes the specific frequency, equivalent to a 24-hour cycle.1)

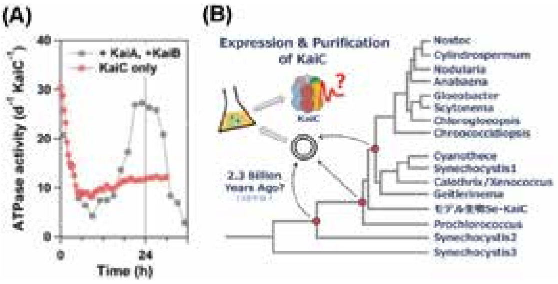

Figure 2. Damped oscillation of KaiC ATPase activity (**A**) and evolutionary diversity of cyanobacteria (**B**).

The habitats of cyanobacteria are diverse, so the space of their sequence is immense.6) Furthermore, some KaiA and KaiB genes are missing in several strains of cyanobacteria. This is understandable to some extent if KaiC possesses the specific frequency. Given our current understanding of this phenomenon, *what specific frequencies are possessed by KaiC homologues in other species and ancestral cyanobacteria?* (Figure 2B) If you strain your ears, the rhythms of the ancient Earth may be heard from beyond evolutionary diversity.

4. Bio-SAXS Activity in IMS7)

We have supported SAXS users so that they can complete experiments smoothly and publish their results.7)

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2) Y. Furuike, A. Mukaiyama, D. Ouyang, K. Ito-Miwa, D. Simon, E. Yamashita, T. Kondo and S. Akiyama, *bioRxiv* doi: 10.1101/2021.08.30.457330 (2021).
3) Y. Furuike, D. Ouyang, T. Tominaga, T. Matsuo, A. Mukaiyama, Y. Kawakita, S. Fujiwara and S. Akiyama, *bioRxiv* doi: 10.1101/2021.08.20.457041 (2021).
4) D. Ouyang, Y. Furuike, A. Mukaiyama, K. Ito-Miwa, T. Kondo and S. Akiyama, *Int. J. Mol. Sci.* **20**, 2789–2800 (2019).
5) K. Ito-Miwa, Y. Furuike, S. Akiyama and T. Kondo, *Proc. Natl. Acad. Sci. U. S. A.* **117**, 20926–20931 (2020). doi: org/10.1073/pnas.2005496117
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7) M. Okumura, S. Kanemura, M. Matsusaki, Y. H. Lee, S. Akiyama and K. Inaba, *Structure* **29**, 1–14 (2021).

Protein Design Using Computational and Experimental Approaches

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Education
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2007 Postdoctoral Fellow, Kyoto Universtiy
2007 JSPS Postdoctoral Fellow for Research Abroad
2009 Postdoctoral Fellow, University of Washington
2014 Associate Professor, Institute for Molecular Science
Associate Professor, The Graduate University for Advanced Studies
2014 JST-PRESTO Researcher (additional post) (–2017)
2018 Associate Professor, Exploratory Research Center on Life and Living Systems (ExCELLS)

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2013 Young Scientist Award, The 51st Annual Meeting of the Biophysical Society of Japan
2018 Morino Foundation for Molecular Science

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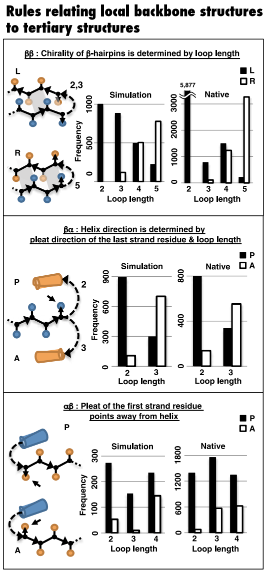
Keywords Protein Design for Structure and Function, Protein Folding, Structural Biology

Protein molecules spontaneously fold into unique three-dimensional structures specified by their amino acid sequences from random coils to carry out their functions. Many of protein studies have been performed by analyzing naturally occurring proteins. However, it is difficult to reach fundamental working principles of protein molecules only by analyzing naturally occurring proteins, since they evolved in their particular environments spending billions of years. In our lab, we explore the principles by computationally designing protein molecules completely from scratch and experimentally assessing how they behave.

Protein design holds promise for applications ranging from catalysis to therapeutics. There has been considerable recent progress in computationally designing new proteins. Many of protein design studies have been conducted using naturally occurring protein structures as design scaffolds. However, since naturally occurring proteins have evolutionally optimized their structures for their functions, implementing new functions into the structures of naturally occurring proteins is difficult for most of cases. Rational methods for building any arbitrary protein structures completely from scratch provide us opportunities for creating new functional proteins. In our lab, we tackle to establish theories and technologies for designing any arbitrary protein structures precisely from scratch. The established methods will open up an avenue of rational design for novel functional proteins that will contribute to industry and therapeutics.



Rules relating local backbone structures to tertiary structures

Selected Publications

- N. Koga, R. Tatsumi-Koga, G. Liu, R. Xiao, T. B. Acton, G. T. Montelione and D. Baker, "Principles for Designing Ideal Protein Structures," *Nature* **491**, 222–227 (2012).
- Y.-R. Lin, N. Koga*, R. Tatsumi-Koga, G. Liu, A. F. Clouser, G. T. Montelione and D. Baker*, "Control over Overall Shape and Size in De Novo Designed Proteins," *Proc. Natl. Acad. Sci. U. S. A.* **112**, E5478–E5485 (2015).

1. Robust Folding of a De Novo Designed Ideal Protein Even with Most of the Core Mutated to Valine

De novo designed ideal proteins, which are stabilized completely consistent local and non-local interactions, exhibit a remarkable property of extremely high thermal stability, compared with naturally occurring proteins. Whereas non-local interactions such as tight hydrophobic core packing have been traditionally considered to be crucial for protein folding and stability, the rules suggest the importance of local backbone structures in protein folding. We studied the robustness of folding of de novo designed proteins to the reduction of the hydrophobic core, by extensive mutation of large hydrophobic residues (Leu, Ile) to smaller ones (Val) for one of the designs. Surprisingly, even after 10-residue mutations from all of Leu and Ile to Val, a mutant with most of the core filled with Val was found to not be a molten globule and fold into the same backbone structure as the original design, with high stability. These results highlight the significance of local backbone structures for the folding ability and high thermal stability of designed proteins.

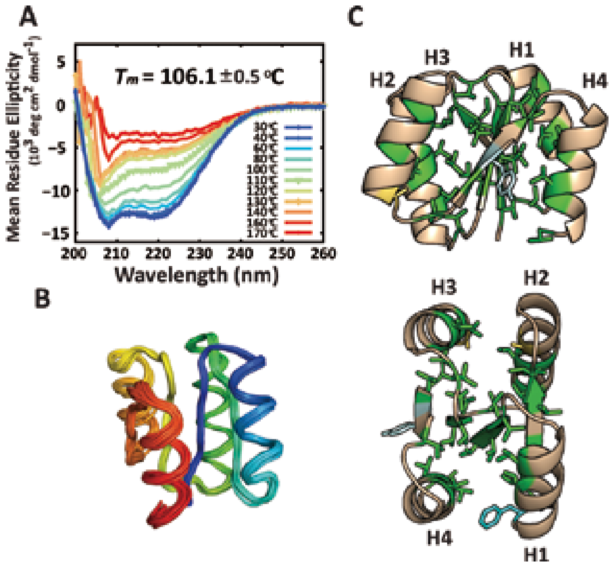


Figure 1. Experimental characterization of the designed protein with most of the core mutated to Val. (A) The far-UV CD spectra at various temperatures. (B) NMR structure. (C) Hydrophobic core side chains are shown in stick. Residues colored in green are valine.

2. Role of Backbone Strain in De Novo Design of Complex α/β Protein Structures

We have elucidated principles for designing ideal proteins with completely consistent local and non-local interactions which have enabled the design of a wide range of new αβ-proteins with four or fewer β-strands. The principles relate local backbone structures to supersecondary-structure packing arrangements of α-helices and β-strands. Here, we test the generality of the principles by employing them to design larger proteins with five- and six- stranded β-sheets flanked by α-helices. The designs are monomeric in solution with high thermal stability, and the nuclear magnetic resonance (NMR) structure of one was close to the design model, but for two others the order of strands in the β-sheet was swapped. Investigation into the origins of this strand swapping suggests that the global structures of the design models are more strained than the NMR structures. We incorporated explicit consideration of global backbone strain into our design methodology, and succeeded in designing proteins with the original unswapped strand arrangements. These results illustrate the value of experimental structure determination in guiding improvement of de novo design, and the importance of consistency between local, supersecondary, and global tertiary interactions in determining protein topology. The augmented set of principles should inform the design of larger functional proteins.

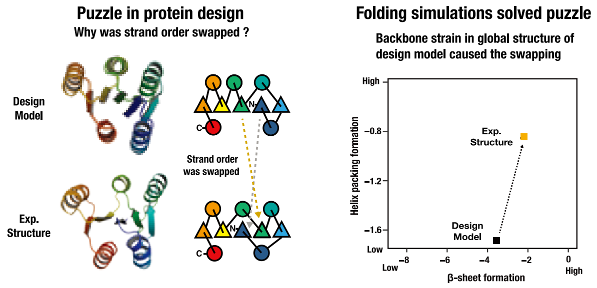


Figure 2. (left) The strand order swapping in de novo design of larger αβ-proteins has been a long-standing problem for the research team. (right) Backbone ensembles generated from folding simulations identified that backbone strain caused the strand swapping.

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2) N. Koga*, R. Koga, G. Liu, J. Castellanos, G. T. Montelione and D. Baker*, *Nat. Commun.* **12**, 3921 (12 pages) (2021).

Awards

KOSUGI, Takahiro; The Young Scientist Excellence Award of Protein Science Society of Japan (PSSJ) (2021).
MITSUMOTO, Masaya; The Poster Excellence Award of the 1st Molecular Engine Workshop (2021).
MITSUMOTO, Masaya; The Poster Award of Protein Science Society of Japan (PSSJ) (2021).
KAIDA, Shingo; The Poster Award of Protein Science Society of Japan (PSSJ) (2021).

Elucidation of Function, Structure, and Dynamics of Condensed-Phase Molecular Systems by Advanced Ultrafast Laser Spectroscopy

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Education

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2013	Ph.D. Tokyo Institute of Technology

Professional Employment

2013	Special Postdoctoral Researcher, RIKEN
2016	Research Scientist, RIKEN
2017	JST-PRESTO Researcher
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Awards

2017	The 8th Research Incentive Award of RIKEN
2017	The Spectroscopical Society of Japan Award for Young Scientists
2019	RSC PCCP Prize
2020	The Commendation for Science and Technology by the Minister of Education, Culture, Sports, Science and Technology The Young Scientists' Award
2020	Morino Foundation for Molecular Science
2020	The 13th Young Scientist Awards of the Japan Society for Molecular Science
2021	The 13th Inoue Science Research Award

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ITO, Atsuko

Keywords Ultrafast Spectroscopy, Nonlinear Spectroscopy, Chemical Reaction Dynamics

We develop and apply advanced ultrafast laser spectroscopy based on state-of-the-art optical technology to study the chemical reaction dynamics of the condensed-phase molecules. In particular, we focus on exploiting unique methodologies based on sub-10-fs pulses (*e.g.*, time-domain impulsive vibrational spectroscopy and multidimensional spectroscopy) and tracking molecular dynamics from electronic and structural viewpoints throughout the chemical reaction with exquisite temporal resolution. We also develop a novel methodology and light source to probe ultrafast dynamics of single molecules in the condensed phase at room temperature, with the aim to understand chemical reaction dynamics at the single-molecule level. Our particular interest rests on elucidating sophisticated molecular mechanisms that underlie the reactions of functional molecular systems such as proteins, molecular assemblies, and metal complexes. On the basis of new insights that can be gained from our advanced spectroscopic approaches, we aim to establish a new avenue for the study of chemical reaction dynamics.

Figure 1. Setup for advanced ultrafast spectroscopy based on sub-10-fs pulses.

Selected Publications

- H. Kuramochi and T. Tahara, "Tracking Ultrafast Structural Dynamics by Time-Domain Raman Spectroscopy," *J. Am. Chem. Soc.* **143**, 9699–9717 (2021).
- H. Kuramochi, S. Takeuchi, M. Iwamura, K. Nozaki and T. Tahara, "Tracking Photoinduced Au–Au Bond Formation through Transient Terahertz Vibrations Observed by Femtosecond Time-Domain Raman Spectroscopy," *J. Am. Chem. Soc.* **141**, 19296–19303 (2019).
- H. Kuramochi, S. Takeuchi, H. Kamikubo, M. Kataoka and T. Tahara, "Fifth-Order Time-Domain Raman Spectroscopy of Photoactive Yellow Protein for Visualizing Vibrational Coupling in Its Excited State," *Sci. Adv.* **5**, eaau4490 (2019).
- H. Kuramochi, S. Takeuchi, K. Yonezawa, H. Kamikubo, M. Kataoka and T. Tahara, "Probing the Early Stages of Photoreception in Photoactive Yellow Protein with Ultrafast Time-Domain Raman Spectroscopy," *Nat. Chem.* **9**, 660–666 (2017).
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- H. Kuramochi, S. Takeuchi and T. Tahara, "Femtosecond Time-Resolved Impulsive Stimulated Raman Spectroscopy Using Sub-7-fs Pulses: Apparatus and Applications," *Rev. Sci. Instrum.* **87**, 043107 (2016).

1. Tracking Ultrafast Dynamics with Time-Domain Raman Spectroscopy

In traditional Raman spectroscopy, narrow-band light is irradiated on a sample, and its inelastic scattering, *i.e.*, Raman scattering, is detected. The energy difference between the Raman scattering and the incident light corresponds to the vibrational energy of the molecule, providing the Raman spectrum that contains rich information about the molecular-level properties of the materials. On the other hand, by using ultrashort optical pulses, it is possible to induce Raman-active coherent nuclear motion of the molecule and to observe the molecular vibration in real time. This time-domain Raman measurement can be combined with femtosecond photo-excitation triggering chemical changes, which enables tracking ultrafast structural dynamics in a form of "time-resolved" time-domain Raman spectroscopy, also known as time-resolved impulsive stimulated Raman spectroscopy (Figure 2). Through our extensive efforts, time-resolved impulsive stimulated Raman spectroscopy now realizes high sensitivity and a wide detection frequency window from THz to 3000 cm^{-1}, and has seen success in unveiling the molecular mechanisms underlying the efficient functions of complex molecular systems. We recently overviewed its application to the study on femtosecond structural dynamics of complex molecular systems such as photoresponsive proteins and molecular assemblies,1) and reported another application to the ultrafast structural dynamics of a fluorescent protein.2) In the latter, we studied excited-state proton transfer (ESPT) dynamics of LSSmOrange, which has been extensively used for multi-color bioimaging owing to its large Stokes shift. The chromophore of LSSm Orange takes a neutral form in the ground state, but the bright orange fluorescence is emitted from the anionic form that is generated through ESPT upon photoexcitation. This ESPT has been known to proceed in a biphasic manner, but its origin has been unknown. We investigated the chromophore structural dynamics during ESPT and unveiled that the chromophore exists in both *trans* and *cis* forms in the ground state, and they are simultaneously photoexcited and undergo ESPT in parallel with significantly different time scales.

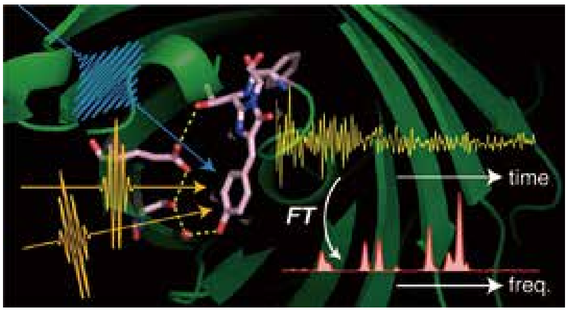

Figure 2. Schematic illustration of time-resolved time-domain Raman spectroscopy. Reprinted with permission from ref. 1. Copyright 2021 American Chemical Society.

2. Generation of Sub-10-fs Pulses with Ultrabroadband Spectral Coverage

Electronic/vibrational coherence has been used as a probe to gain detailed insights into the chemical reaction dynamics. Moreover, it has recently attracted tremendous interest as a control knob for directing and thus enhancing chemical reactions in the desired way. Observing and manipulating such coherences of the condensed phase polyatomic molecules inevitably require extremely short pulses with broad spectral coverage to monitor relevant electronic transitions thoroughly. Nevertheless, generating such ultrashort pulses has been primarily limited in the visible spectral region from the viewpoint of spectroscopic applications, where long-term high stability is required. We developed light sources to generate highly stable sub-10-fs pulses in a broad spectral coverage from UV to NIR. The light source is based on a Yb:KGW regenerative amplifier. Through various nonlinear optical processes such as optical parametric amplification, self-phase modulation, and subsequent sum-frequency mixing, we generate pulses tunable from 300–1400 nm with bandwidths that support the pulse duration well below 10 fs at Fourier transform limit, as shown in Figure 3. We compensate group delay dispersion of these pulses by a combination of chirped mirrors and a pulse shaper, and the intensity profiles of the compressed pulses retrieved from Frequency-Resolved Optical Gating (FROG) measurement show that the compressed pulses have a pulse duration as short as 4.5 fs. Applications of these pulses to ultrafast spectroscopy of functional molecules are now in progress.

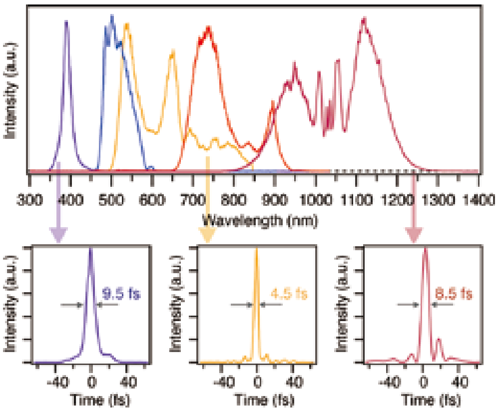

Figure 3. (Top) Typical spectra of the broadband pulses that support Fourier transform limit pulse duration of <10 fs. (Bottom) Intensity profiles of the compressed pulses retrieved from the FROG data.

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1) H. Kuramochi and T. Tahara, *J. Am. Chem. Soc.* **143**, 9699–9717 (2021).
2) P. Kumar, E. Fron, H. Hosoi, H. Kuramochi, S. Takeuchi, H. Mizuno and T. Tahara, *J. Phys. Chem. Lett.* **12**, 7466–7473 (2021).

Awards

KURAMOCHI, Hikaru; The 13th Inoue Science Research Award (2021).
KURAMOCHI, Hikaru; The 13th Young Scientist Awards of the Japan Society for Molecular Science (2020).

Open up Future Electronics by Organic Molecules

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2000 Research Scientist, RIKEN
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2012 Professor, Institute for Molecular Science
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Awards
2009 RSC Publishing CrystEngComm Prize
2009 Young Scientist Awards, Japan Society for Molecular Science
2010 RIKEN-ASI Award for the Young Scientist
2019 The CSJ Award for Creative Work
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SUZUKI, Ai
ISHIKAWA, Yuko

Keywords Organic Mott Insulator, Field Effect Transistors, Organic Spintronics

Organic molecules are attracting recent attention as new ingredients of electronic circuits. Our group focuses on the development of organic electronics in the next era by providing new mechanism and concepts of the device operation and fabrication. For example, an electronic phase transition is utilized for the ON/OFF switching of our field-effect-transistor (FET). This special FET is called an organic Mott-FET, where the conduction electrons in the organic semiconductor are solidified at the OFF state because of Coulomb repulsion among carriers. In the operation, these solidified electrons can be melted by applying a gate voltage, and show an insulator-to-metal transition so-called Mott-transition to be switched to the ON state. Because of this phase transition, a large electric response of the device can be achieved, resulting in the highest device mobility ever observed for organic FETs. In addition to this high performance, the Mott-FET is interesting in terms of superconductivity. Because the Mott-transition sometimes accompanies superconducting phase in between metal and insulator, modulation of gate electric field at low temperature may induce superconductivity. In fact, we have achieved first example of field-induced superconductivity in an organic FET. By combining a strain effect that can tune the bandwidth, this type of electric-field-induced superconducting transition can be utilized for mapping the phase diagram around the Mott-insulator as shown in Figure 1.

Another approach to the future electronics is the development of spintronic devices based on chirality of organic material. We aim to implement chirality-induced spin selectivity (CISS) effect into molecular devices that can generate spin-polarized current. This type of device is expected to realize spintronics devices without magnet or topological insulator.

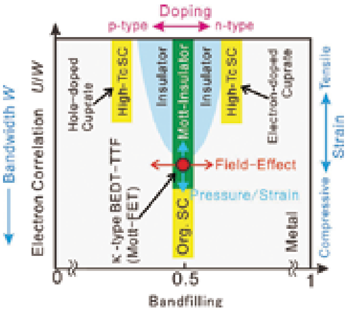

Figure 1. Phase diagram surrounding a Mott-insulator. SC denotes superconductor, while *U* and *W* are on-site Coulomb repulsion and bandwidth, respectively.

Selected Publications

- H. M. Yamamoto, "Phase-Transition Transistor Based on Organic Mott Insulators," *Bull. Chem. Soc. Jpn.* **94**, 2505–2539 (2021).
- Y. Kawasugi, K. Seki, S. Tajima, J. Pu, T. Takenobu, S. Yunoki, H. M. Yamamoto and R. Kato, "Two-Dimensional Ground-State Mapping of a Mott-Hubbard System in a Flexible Field-Effect Device," *Sci. Adv.* **5**, eaav7282 (9 pages) (2019).
- M. Suda, Y. Thathong, V. Promarak, H. Kojima, M. Nakamura, T. Shiraogawa, M. Ehara and H. M. Yamamoto, "Light-Driven Molecular Switch for Reconfigurable Spin Filters," *Nat. Commun.* **10**, 2455 (7 pages) (2019).
- M. Suda, R. Kato and H. M. Yamamoto, "Light-Induced Superconductivity Using a Photo-Active Electric Double Layer," *Science* **347**, 743–746 (2015).

1. Current-Induced Spin-Polarization in a Chiral Crystal $CrNb_3S_6$ [1,2]

CISS effect has remarkable ability which generates highly polarized spin current even with light element molecules. However, its extension to inorganic chiral materials has not been well investigated. Moreover, detection of CISS effect in metals that show ohmic response is quite interesting because one can discuss the CISS-based spin polarization in terms of band theory if metallic CISS effect in linear response regime is observed. So far, however, CISS experiments have been investigated only in tunnelling conduction regime.

We detected CISS-based spin transport phenomena in a monoaxial chiral dichalcogenide $CrNb_3S_6$. This material has chiral structure and metallic conduction, so that we could perform CISS experiments with metallic conduction regime. Spin polarization was detected in this chiral bulk crystal under a charge current flowing along the principal *c* axis at room temperature without magnetic field. The detection was made by an inverse spin Hall signal which is induced on the tungsten electrode that absorbs polarized spin from the chiral crystal. An inverse response was also observed when applying the charge current into the tungsten electrode, which implied an inverse CISS effect. The signal sign reversed in the device with the opposite chirality, which is consistent with the symmetry required for CISS effect. Furthermore, the spin signals were found over micrometer length scale in a nonlocal configuration. Such a robust generation and protection of the spin-polarized state can be discussed based on a one-dimensional model with an antisymmetric spin–orbit coupling.

In addition to the above experiments, we also detected bulk magnetization generated by applying electric current to the crystal using SQUID magnetometer (Figure 2). When the current amplitude was swept from negative to positive, the current-induced magnetization changed linearly. Directly detecting such magnetization by magnetometry enables one to estimate the number of spin-polarized electrons. Using this number, we evaluated the spin polarization rate within the framework of Boltzmann's equation and found that spin polarization generated by CISS effect was enhanced by 10^5 times inside this material. It seemed that effective magnetic field generated by CISS could reach 10^3 T at high current density, which again confirmed the robustness of CISS effect. We also observed that the current-induced magnetization increased in the vicinity of the phase boundary between paramagnetic and forced ferromagnetic phases, which could be attributed to the spin fluctuation associated with the phase transition. (SQUID = superconducting quantum interference device)

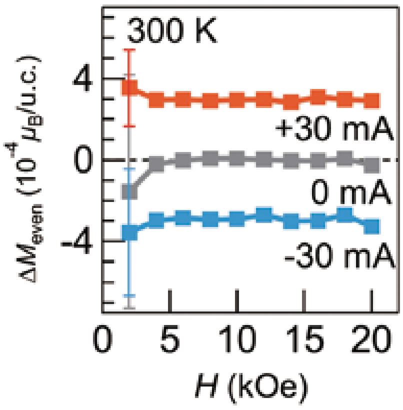

Figure 2. Detection of spin polarization in a chiral metal $CrNb_3S_6$. By applying electrical current, electron spins are polarized along the current direction by CISS effect. The amplitude of the magnetization is irrelevant to the applied magnetic field, which strongly supports the current-induced nature of this magnetization.

2. Spin Current Generation in a Chiral Organic Superconductor

Although centrosymmetric *s*- and *d*-wave superconductors are in a spin singlet state, a superconductor with broken mirror symmetry is expected to show spin triplet state, according to a theory developed by Edelstien.[3] This means spin polarization can be generated by applying supercurrent in a chiral superconductor, whose magnetization direction depending on the lattice symmetry has been recently calculated by group theory.[4] We have tested this idea by employing κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ (hereafter, κ-NCS) which is an organic superconductor with chiral and polar crystal lattice. The space group of this crystal is $P2_1$, and its handedness is defined by the relative arrangement between the anionic Cu(NCS)$_2$ and cationic BEDT-TTF. This handedness can be experimentally determined by X-ray diffraction or circular dichroism. After confirming pure enantiomeric lattice system, a thin crystal of κ-NCS has been laminated onto a resin substrate with prepatterned gold and nickel electrodes. At temperature lower than superconducting *T*c, an electrical current was applied to induce spin magnetization. The spin polarization accumulated at the interface between κ-NCS and the magnetic electrode was detected as a voltage that is dependent on the magnetic field. By measuring the angle dependency of this magnetovoltaic signal, the direction of accumulated spin could be determined. The spin polarization direction was dependent on the specific location inside the crystal, and its arrangement was consistent with a magnetic quadrupole structure which has been hypothesized in a chiral molecule with CISS effect.
[BEDT-TTF = bis(ethylenedithio)tetrathiafulvalene]

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* IMS International Internship Program

RESEARCH ACTIVITIES

Center for Mesoscopic Sciences

In the past few decades, great progress in experimental and theoretical methods to analyze structures, dynamics, and properties of single-component (or single hierarchical) molecules and nanomaterials has been made. Now we should also direct our attention to properties and functions of multi-hierarchical molecular systems. We develop innovative methods of measurements and analysis for molecular and materials systems to elucidate the processes that trigger the functions and reactions of the systems in the mesoscopic regime, that is the regime where micro and macroscopic properties influence each other.

Nano-Optical Imaging and Application to Nanomaterials

Center for Mesoscopic Sciences
Division of Supersensitive Measurements

OKAMOTO, Hiromi
Professor
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Education

1983	B.S. The University of Tokyo
1991	Ph.D. The University of Tokyo

Professional Employment

1985	Research Associate, Institute for Molecular Science
1990	Research Associate, The University of Tokyo
1993	Associate Professor, The University of Tokyo
2000	Professor, Institute for Molecular Science Professor, The Graduate University for Advanced Studies

Award

2012	The Chemical Society of Japan (CSJ) Award for Creative Work
2020	The Commendation for Science and Technology by the MEXT Awards for Science and Technology Research Category

Member
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YOSHIZAWA, Daichi
Project Assistant Professor (NINS)
AHN, Hyo-Yong
Post-Doctoral Fellow
YAMANISHI, Junsuke
Technical Fellow
ISHIKAWA, Akiko
Secretary
NOMURA, Emiko

Keywords Nano Optics, Plasmons, Chirality

Studies of local optical properties of molecular assemblies and materials are the keys to understanding nanoscale physical and chemical phenomena, and for construction of nanoscale functional devices. Nano-optical methods, such as scanning near-field optical microscopy (SNOM), enable optical imaging with spatial resolution beyond the diffraction limit of light. Combination of nano-optical techniques with various advanced spectroscopic methods may provide a methodology to analyze nanoscale functionalities and dynamics directly. It may yield essential and basic knowledge to understand origins of characteristic features of the nanomaterial systems. We have constructed nano-optical (near-field and far-field) spectroscopic and microscopic measuring systems, for the studies on excited-state properties of nanomaterials, with the feasibilities of nonlinear and time-resolved measurements. The developed apparatuses enable nano-optical measurements of two-photon induced emission, femtosecond time-resolved signals, and chiro-optical properties (as typified by circular dichroism), in addition to conventional transmission, emission, and Raman-scattering. Based on these methods, we are investigating the characteristic spatial and temporal behavior of various metal-nanostructure systems and molecular assemblies. Typical examples are shown in Figure 1. We succeeded in visualizing wave functions of resonant plasmon modes in single noble metal nanoparticles, confined optical fields in noble metal nanoparticle assemblies. In the past several years, we succeeded in observing plasmon wave packet propagation dynamics with ultrafast time-resolved near-field imaging, local chiro-optical properties of chiral and achiral metal nanostructures, and so forth. We also developed far-field high-precision circular dichroism microscope that facilitate chirality analysis of materials in a wide range of research areas. The information on nano-optical properties of the materials are also relevant to exploration of novel optical manipulation principles, which is another research topic of the research group.

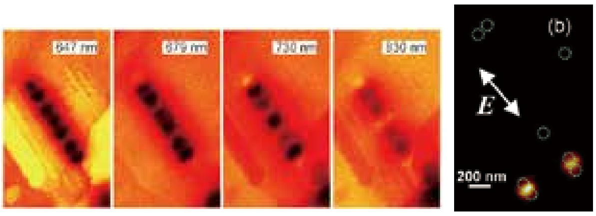

Figure 1. (Left four panels) Near-field transmission images of gold nanorod (20 nm^D × 510 nm^L). The wavelengths of observation were 647, 679, 730, and 830 nm from left to right. The spatial oscillating features were attributed to the square amplitudes of the resonant plasmonic wave functions. (Right) Near-field two-photon excitation image of dimers of spheric gold nanoparticles (diameter 100 nm) observed at 785 nm. The arrows indicates the incident light polarization. Dotted circles represent approximate positions of the particles.

Selected Publications

- H. Okamoto, “Local Optical Activity of Nano- to Microscale Materials and Plasmons,” *J. Mater. Chem. C* **7**, 14771–14787 (2019).
- H. Okamoto, T. Narushima, Y. Nishiyama and K. Imura, “Local Optical Responses of Plasmon Resonance Visualized by Near-Field Optical Imaging,” *Phys. Chem. Chem. Phys.* **17**, 6192–6206 (2015).
- H. Okamoto and K. Imura, “Visualizing the Optical Field Structures in Metal Nanostructures,” *J. Phys. Chem. Lett.* **4**, 2230–2241 (2013).

1. Supramolecular Chirality Synchronization in Thin Films of Plasmonic Nanocomposites[1)]

Mirror symmetry breaking (chirality) in materials is a fascinating phenomenon that has practical implications for various optoelectronic technologies. Chiral plasmonic materials are particularly appealing due to their strong and specific interactions with light. In this work we broaden the portfolio of available strategies toward the preparation of chiral plasmonic assemblies, by applying the principles of chirality synchronization—a phenomenon known for small molecules, which results in the formation of chiral domains from transiently chiral molecules. We report the controlled co-crystallization of 23 nm gold nanoparticles and liquid crystal molecules yielding domains made of highly ordered, helical nanofibers, preferentially twisted to the right or to the left within each domain. We applied our recently developed precise far-field circular dichroism (CD) microscopy to this system and confirmed that such micrometer sized domains exhibit strong CD signals, even though the bulk material is racemic. We further highlight the potential of the proposed approach to realize chiral plasmonic thin films by using a mechanical chirality discrimination method. Toward this end, we utilized a rapid CD imaging technique based on the use of polarized optical microscopy, which enabled probing the CD signal. The method allows us to extend intrinsically local effects of chiral synchronization to the macroscopic scale, thereby broadening the available tools for chirality manipulation in chiral plasmonic systems.

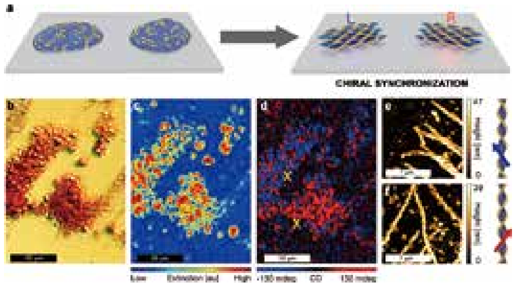

Figure 2. Micrometer-scale circular dichroism measurements of the helical Au nanoparticle assemblies.[1)] (a) Graphical representation of the chiral synchronization process. (b) Optical micrograph, (c) extinction intensity map at 550 nm, and (d) CD map at 550 nm from the same region of the sample. (e) AFM height map of a selected region from a left-handed and (f) a right-handed domain, with graphical models of the helical nanofilament. ©ACS 2020

2. Directional Supramolecular Polymerization to Form Nanofibers in a Microflow Reaction System[2,3)]

Directional chain reactions are common self-assembly processes in nature. However, it has been challenging to achieve such processes in artificial one-dimensional self-assembling systems. In this work, we conducted supramolecular polymerization of perylene bisimide derivatives to form nanofibers. With selectively activating one end of a supramolecular polymer during its growth in a microflow channel, it realized directional supramolecular polymerization. The dependency of the aggregation efficiency on the flow rate suggested that the shear force facilitated collisions among the monomers to overcome the activation energy required for nucleation. By introducing a solution containing both monomer and polymer, we investigated how the shear force influenced the monomer–polymer interactions. In situ fluorescence spectra and microscopic absorption linear dichroism measurements in the microflow system revealed that growth of the polymers was accelerated only when they were oriented under the influence of shear stress. Upon linear motion of the oriented polymer, polymer growth at that single end became predominant relative to the nucleation of freely diffusing monomers. This strategy—friction-induced activation of a single end of a polymer—should be applicable more generally to directional supramolecular block co-polymerizations of various functional molecules, allowing molecular heterojunctions to be made at desired positions in a polymer.

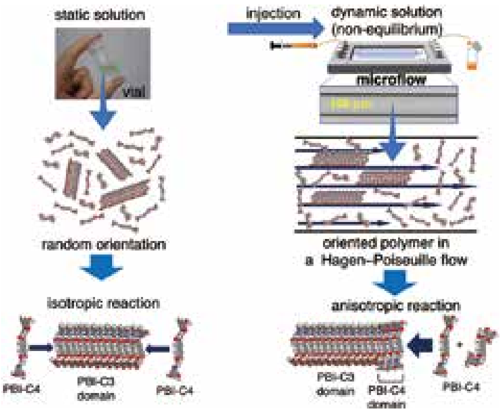

Figure 3. Comparison of general isotropic supramolecular polymerization in a vial (left) and the directional anisotropic supramolecular polymerization in a microflow system (right).[2)] In the microflow system, the forward-facing terminus of the highly aligned polymer reacts with monomers, thereby leading to anisotropic elongation. ©ACS 2021

3. Optical Trapping of Chiral Metal Nanoparticles

Optical trapping experiments of chiral metal nanoparticles with circularly polarized light were conducted. The analysis of the data to reveal the origin of dissymmetry in optical force is now in progress.

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1) P. Szustakiewicz, N. Kołsut, D. Grzelak, T. Narushima, M. Góra, M. Bagiński, D. Pociecha, H. Okamoto, L. M. Liz-Marzán and W. Lewandowski, *ACS Nano* **14**, 12918–12928 (2020).

2) S. Matoba, C. Kanzaki, K. Yamashita, T. Kusukawa, G. Fukuhara, T. Okada, T. Narushima, H. Okamoto and M. Numata, *J. Am. Chem. Soc.* **143**, 8731–8746 (2021).

3) C. Kanzaki, S. Matoba, A. Inagawa, G. Fukuhara, T. Okada, T. Narushima, H. Okamoto and M. Numata, *Bull. Chem. Soc. Jpn.* **94**, 579–589 (2021).

Atomic-Scale Optical Spectroscopy

Center for Mesoscopic Sciences
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Education

2006	B.S. Ritsumeikan University
2008	M.S. Kyoto University
2011	Ph.D. Kyoto University

Professional Employment

2008	JSPS Research Fellow, Kyoto University
2011	JSPS Research Fellow, Fritz-Haber Institute
2013	Group Leader, Fritz-Haber Institute
2021	Associate Professor, Institute for Molecular Science Associate Professor, The Graduate University for Advanced Studies
2020	Guest Professor, Hokkaido University

Awards

2013	Inoue Research Award for Young Scientists
2014	Morino Award for Molecular Science
2016	Gerhard Ertl Young Investigator Award
2020	Gaede Prize (German Physical Society)
2020	The Commendation for Science and Technology by the Minister of Education, Culture, Sports, Science and Technology The Young Scientists' Award
2020	Heinrich Rohrer Medal (The Japan Society of Vacuum and Surface Science)

Member
Assistant Professor
NISHIDA, Jun
Secretary
ITO, Atsuko

Keywords Atomic-Scale Optical Spectroscopy, Scanning Probe Microscopy, Nanoscale Science

Optical imaging and spectroscopy at atomic resolution is an overarching goal in modern nanoscale science and technology, allowing us to directly access atomic-scale structures and dynamics in real space and real time. Atomic-scale crystal imperfections, defects and inhomogeneities indeed play a crucial role in physicochemical properties and functions of solid catalysts and semiconductor optoelectronic devices. We have challenged to attain atomic-scale optical spectroscopy by combining advanced low-temperature scanning tunneling microscopy, laser spectroscopy and nanoplasmonics.

Electromagnetic fields can be confined to nanoscale through excitation of localized surface plasmon resonances of metallic nanostructures. Plasmonics is a mature research field, enabling precise control of nanoscale light. Accordingly, nanoscale optical imaging and spectroscopy well below the diffraction limit has become a more routine technique. However, the typical spatial resolution remains a few tens of nanometers, which is still far from the atomistic length scale. More recently, state-of-the-art experiments and theories demonstrated that atomic-scale confinement of electromagnetic fields occurs at atomistic asperities existing on metallic nanostructures. However, it is an outstanding challenge to precisely manipulate atomically confined light. We have developed advanced experimental techniques to manipulate extremely confined, strong plasmonic fields in scanning tunneling microscope junctions and implemented ultrasensitive and ultrahigh resolution optical spectroscopy. We also investigate intriguing atomic-scale strong light–matter interactions in an atomically well-defined environment.

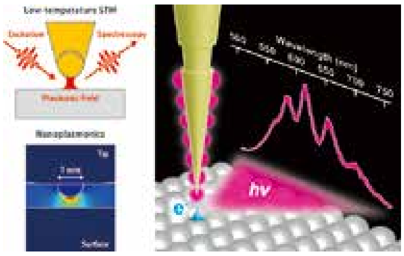

Figure 1. Atomic-scale optical spectroscopy in plasmonic scanning probe microscope junction.

Selected Publications

- S. Liu *et al.*, "Plasmon-Assisted Resonant Electron Tunneling in a Scanning Tunneling Microscope Junction," *Phys. Rev. Lett.* **121**, 226802 (2018).
- H. Böckmann, S. Liu *et al.*, "Near-Field Manipulation in a Scanning Tunneling Microscope Junction with Plasmonic Fabry-Pérot Tips," *Nano Lett.* **19**, 3597–3602 (2019).
- S. Liu *et al.*, "Resolving the Correlation between Tip-Enhanced Resonance Raman Scattering and Local Electronic States with 1 nm Resolution," *Nano Lett.* **19**, 5725–5731 (2019).
- S. Liu *et al.*, "Dramatic Enhancement of Tip-Enhanced Raman Scattering Mediated by Atomic Point Contact Formation," *Nano Lett.* **20**, 5879–5884 (2020).
- S. Liu *et al.*, "Atomic Point Contact Raman Spectroscopy of a Si(111)-7×7 Surface," *Nano Lett.* **21**, 4057–4061 (2021).
- S. Liu *et al.*, "Anti-Stokes Light Scattering Mediated by Electron Transfer Across a Biased Plasmonic Nanojunction," *Nano Lett.*, in print.

1. Control of Gap-Mode Plasmons in Scanning Tunneling Microscope Junctions

Optical imaging and spectroscopy in plasmonic scanning tunneling microscope junctions rely on gap-mode plasmons whose properties are largely determined by the nanoscale morphology of the tip apex. Although a metallic tip for a scanning tunneling microscope is typically prepared by electrochemical etching, it is hard to precisely control the nanoscale structure of its apex. In order to obtain plasmonic tips in a highly controlled and reproducible manner, we employed focused ion beam milling.1) Figure 2a displays a scanning electron micrographs of a gold tip with a nanoscopically sharpened apex. Furthermore, we demonstrated that the spectral features of the gap-mode plasmon can be controlled by making nanoscale structures on the tip shaft. As an exemplary case, we produced nanoscopically sharp gold tips with a single groove on the shaft at a distance of a few micrometers from the apex. This structure leads to tunable plasmonic Fabry–Pérot interference. Figures 2b and 2c show the electrodynamic simulation and the scanning tunneling luminescence spectra, respectively, where the modulated spectral response through the interference is observed. Nanofabrication of plasmonic tips will be a key technology to attain highly precise, reproducible nanoscale and atomic-scale optical imaging and spectroscopy.

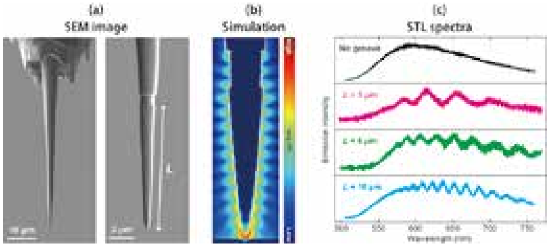

Figure 2. Nanofabrication of plasmonic tip with focused ion beam milling. (a) Scanning electron micrograph of a nanoscopically sharpened gold tip. (b) Simulation of plasmonic Fabry–Pérot tip. (c) Scanning tunneling luminescence spectra of the plasmonic Fabry–Pérot tip.

2. Ultrasensitive and Ultrahigh Resolution Tip-Enhanced Raman Spectroscopy

Raman spectroscopy is a versatile tool widely used in physics, chemistry and biology. Low-temperature tip-enhanced Raman spectroscopy (TERS) enables chemical identification with single-molecule sensitivity and with extremely high spatial resolution even down to the atomic scale.2,3) The large enhancement of Raman scattering obtained in TERS originates from electromagnetic field and/or chemical enhancement mechanisms. Whereas former enhancement requires a strong near-field through excitation of localized surface plasmons, the latter is governed by resonance in the electronic structure of the sample, known as resonance Raman spectroscopy. Recently we demonstrated tip-enhanced resonance Raman scattering (TERRS) for ultrathin ZnO films epitaxially grown on a Ag(111) surface,4) where both electromagnetic and chemical enhancement mechanisms are simultaneously operative, yielding exceptionally high sensitivity. By recording scanning tunneling spectroscopy (STS) in parallel, we also showed that the TERRS intensity is strongly correlated with the nanoscale variation of the electronic resonance. It was found that the spatial resolution of TERRS is dependent on the tip–surface distance and reaches nearly 1 nm in the tunneling regime. This exceptionally high resolution can be rationalized by the extreme confinement of the plasmonic field in the junction. Simultaneous STS and TERRS mapping visualize a correlation between the local electronic resonance and the Raman spectrum at near-atomic resolution. Therefore, TERRS will pave the way to directly observe electron–phonon coupling on the atomic length scale.

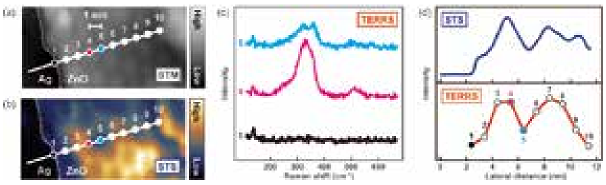

Figure 3. Tip-enhanced resonance Raman spectroscopy of ultrathin zinc oxide films. (a) and (b) STM and STS images of ultrathin zinc oxide film. (c) TERRS spectra obtained at different locations over the zinc oxide film. (d) STS and TERRS intensities along the line indicated in (a) and (b).

Additionally, we discovered that tip-enhanced Raman scattering can be dramatically enhanced through formation of atomic point contacts.5,6) We showed that atomic point contact formation between a silver tip and the surface of a bulk Si sample can lead to the dramatic enhancement of Raman scattering and consequently the phonon modes of the reconstructed Si(111)-7×7 surface can be detected. Furthermore, we demonstrate the chemical sensitivity of this method by probing local vibrations resulting from Si–O bonds on the partially oxidized Si(111)-7×7 surface. This approach will expand the applicability of ultrasensitive tip-enhanced Raman spectroscopy, exceeding the previous measurement strategies that exploit intense gap-mode plasmons, typically requiring a plasmonically resonant substrate.

References

1) H. Böckmann, S. Liu *et al.*, *Nano Lett.* **19**, 3597 (2019).
2) J. Lee *et al.*, *Nature* **568**, 78 (2019).
3) Y. Zhang *et al.*, *Natl. Sci. Rev.* **6**, 1169–1175 (2019).
4) S. Liu *et al.*, *Nano Lett.* **19**, 5725 (2019).
5) S. Liu *et al.*, *Nano Lett.* **20**, 5859 (2020).
6) S. Liu *et al.*, *Nano Lett.* **21**, 4057 (2021).

Awards

KUMAGAI, Takashi; Gaede Prize (German Physical Society) (2020).
KUMAGAI, Takashi; Heinrich Rohrer Medal (The Japan Society of Vacuum and Surface Science) (2020).

Center for Mesoscopic Sciences as an Interdepartmental Facility

OKAMOTO, Hiromi	Director, Professor
OHMORI, Kenji	Professor
IINO, Ryota	Professor
EHARA, Masahiro	Professor
SUGIMOTO, Toshiki	Associate Professor
MINAMITANI, Emi	Associate Professor
KUMAGAI, Takashi	Associate Professor
NARUSHIMA, Tetsuya	Assistant Professor
YOSHIZAWA, Daichi	Assistant Professor
NISHIDA, Jun	Assistant Professor
OKANO, Yasuaki	Technical Associate
NOMURA, Emiko	Secretary

As the succeeding organization of former Laser Research Center for Molecular Science, Center for Mesoscopic Sciences continues development of new experimental apparatus and methods to open groundbreaking research fields in molecular science, in collaboration with other departments and facilities. Those new apparatus and methods will be served as key resources in advanced collaboration with the researchers from the community of molecular science. The targets cover:

- novel quantum-control schemes based on intense and ultrafast lasers
- novel optical imaging and nanometric microscopy and spectroscopy
- novel method of analysis for mesoscopic phenomena

and so forth.

The Center also possesses several general-purpose instruments for laser-related measurements (commercial as well as in-house developed), and lends them to researchers in IMS who conduct laser-based studies, so as to support and contribute to their advanced researches.

RESEARCH ACTIVITIES

Division of Advanced Molecular Science

The division consists of two sections. In the first one, scientists of the first water are invited as "distinguished professors," and the environment, in which they can devote themselves to their own research, is provided. The research in this section should be the last word in the field of molecular science.

In the second section, we invite researchers in the universities performing unique researches in the field of molecular science as cross-appointment faculty members, and provide the research environment to enable research activity with advanced facilities in IMS.

Self-Assembling Molecular Systems Based on Coordination Chemistry

Division of Advanced Molecular Science

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Education

1980	B.S. Chiba University
1982	M.S. Chiba University
1987	Ph.D. Tokyo Institute of Technology

Professional Employment

1982	Researcher, Sagami Chemical Research Center
1988	Assistant Professor to Associate Professor, Chiba University
1997	Associate Professor, Institute for Molecular Science
1999	Professor, Nagoya University
2002	Professor, The University of Tokyo
2018	Distinguished Professor, Institute for Molecular Science
2019	Distinguished Professor, The University of Tokyo

Awards

1994	Progress Award in Synthetic Organic Chemistry, Japan
2000	Division Award of Chemical Society of Japan (Organic Chemistry)
2001	Tokyo Techno Forum 21 Gold Medal
2001	Japan IBM Award
2003	Nagoya Silver Medal
2004	Izatt-Christensen Award
2006	G. W. Wheland Award (Chicago University Lectureship Award)
2010	The Reona Esaki Award
2010	The JSCC Award
2011	3M Lectureship Award (University of British Columbia)
2012	Thomson Reuters Research Front Award 2012
2013	The Chemical Society of Japan (CSJ) Award
2013	Arthur C. Cope Scholar Award (ACS National Award)
2013	Merck-Karl Pfister Visiting Professorship (MIT Lectureship Award)
2014	ISNSCE 2014 Nanoprize
2014	Medal with Purple Ribbon
2014	Fred Basolo Medal (Northwestern University)
2018	Wolf Prize in Chemistry
2019	The Imperial Prize and the Japan Academy Prize
2020	The 73rd Chunichi Cultural Award
2020	Clarivate Citation Laureates (Chemistry)
2020	"Major Results" of Nanotechnology Platform, MEXT

Member
IMS Research Assistant Professor
MITSUHASHI, Takaaki
Visiting Scientist
TAKATA, Yusuke
GONDO, Keisuke
Graduate Student
CHEN, Jiazhuo*
WADA, Naoki*
ZHOU, Boyu*
JUNG, Youngcheol*
Secretary
MASUDA, Michiko

Keywords Self-Assembly, Nano-Space, Coordination Chemistry

We are designing new self-assembled molecular systems based on coordination chemistry, and trying to apply the molecular system to various research fields.

For example, we applied the self-assembled molecular systems to biological studies and the structure elucidation of small molecules (Figures 1 and 2).

Currently, we are focusing on the following two projects:

(1) Protein encapsulation in self-assembled Coordination cages: In this project, we aim to explore the potential of proteins encapsulated within precisely designed molecular capsules (Figure 1). We envision to 1) control the property of protein (*e.g.*, stability, ligand affinity or selectivity), 2) control enzymatic reactivity (*e.g.*, activity or new function), and 3) develop new analytical methodology (coupled with NMR, X-ray, MS or cryoEM *etc.*).

(2) Crystalline sponge (CS) method: The CS is a porous crystal, which can accommodate various kinds of small molecules, and align the accommodated molecules neatly in its inner space. Actually, we can observe the structure of the small molecules neatly aligned in the CS by the X-ray crystallography (Figure 2). The method has a potential to accelerate the various kinds of researches, in which the structure elucidation of novel compounds is required. We target to develop new drug discovery using this method.

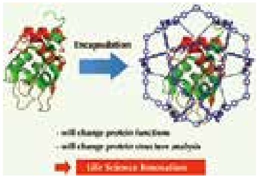

Figure 1. Cartoon presentation for the protein encapsulation.

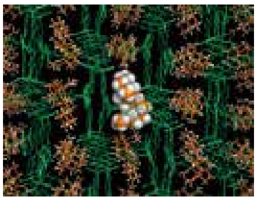

Figure 2. One example of the crystalline sponge methode.

Selected Publications

- Y. Inokuma, S. Yoshioka, J. Ariyoshi, T. Arai, Y. Hitora, K. Takada, S. Matsunaga, K. Rissanen and M. Fujita, "X-Ray Analysis on the Nanogram to Microgram Scale Using Porous Complexes," *Nature* **495**, 461–466 (2013).
- D. Fujita, Y. Ueda, S. Sato, N. Mizuno, T. Kumasaka and M. Fujita, "Self-Assembly of Tetravalent Goldberg Polyhedra from 144 Small Components," *Nature* **540**, 563–566 (2016).

1. Protein Stabilization and Refolding in a Gigantic Self-Assembled Cage

Spatial isolation of molecules is often a powerful strategy for regulating their molecular behavior. Biological systems employ such mechanisms well; however, scientists have yet to rival nature, particularly for macromolecular substrates. We demonstrated that the encapsulation of a protein in a molecular cage with an open framework stabilizes the tertiary structure of the protein and improves its enzymatic activity. Particularly, when the three-dimensionally confined enzyme was exposed to an organic solvent, its half-life was prolonged 1,000-fold. Kinetic and spectroscopic analysis of the enzymatic reaction revealed that the key to this stability is the isolated space; this is reminiscent of chaperonins, which use their large internal cavities to assist the folding of client proteins (Figure 3). The single-molecule protein caging affords a new type of protein-based nanobiotechnology that accelerates molecular biology research as well as industrial applications.

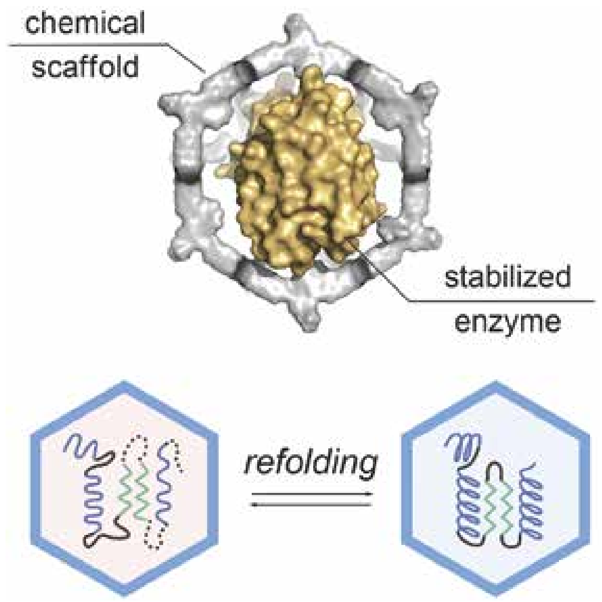

Figure 3. Protein refolding in the cage.

2. Absolute Configuration Determination from Low *ee* Compounds by the Crystalline Sponge Method

When chiral compounds with low enantiomeric excess (*ee*, R:S = m:n) were absorbed into the void of the CS, enantiomerically pure $[(R)_m(S)_n]$ chiral composites were formed, changing the centrosymmetric space group into non-centrosymmetric one (Figure 4). The absolute configuration of the analyte compounds was elucidated with a reasonable Flack (Parsons) parameter value. This phenomenon is characteristic to the "post-crystallization" in the pre-determined CS crystalline lattice, seldom found in common crystallization where the crystalline lattice is defined by an analyte itself. The results highlight the potential of the CS method for absolute configuration determination of low ee samples, an often encountered situation in asymmetric synthesis studies, which is important for the development of new drugs.

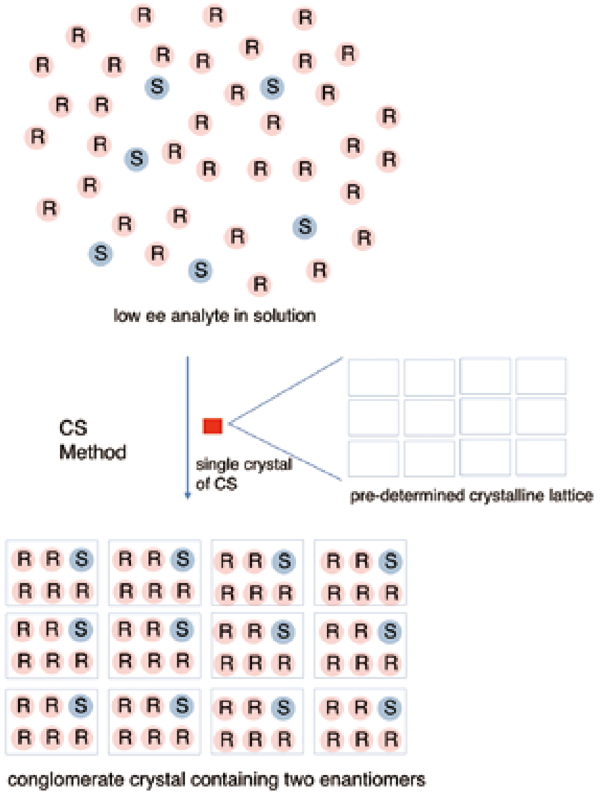

Figure 4. CS method was applied to the analysis of chiral compounds with low enantiomeric excess.

References

1) D. Fujita, R. Suzuki, Y. Fujii, M. Yamada, T. Nakama, A. Matsugami, F. Hayashi, J.-K. Weng, M. Yagi-Utsumi and M. Fujita, *Chem* **7**, (2021), in press.
2) R. Dubey, K. Yan, T. Kikuchi, S. Sairenji, A. Rossen, S. S. Goh, B. L. Feringa and M. Fujita, *Angew. Chem., Int. Ed.* **60**, 11809–11813 (2021).

Awards

FUJITA, Makoto; Clarivate Citation Laureates (Chemistry) (2020).
MITSUHASHI, Takaaki; FUJITA, Makoto; "Major Results" of Nanotechnology Platform, MEXT (2020).

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* carrying out graduate research on Cooperative Education Program of IMS with the University of Tokyo

Exploring Novel Physical Properties by Multi-Dimensional Spectroscopy

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(Department of Materials Molecular Science, Electronic Structure)

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Education

1988	B.S. Tohoku University
1990	M.S. Tohoku University
1991	Ph.D. Tohoku University

Professional Employment

1991	JSPS Postdoctoral Fellow, Tohoku University
1993	Research Associate, Kobe University
1993	Research Associate, Institute for Molecular Science
1998	Associate Professor, Kobe University
2002	Associate Professor, Institute for Molecular Science
2013	Professor, Osaka University
2020	Professor (Cross Appointment), Institute for Molecular Science

Awards

2001	Young Incentive Award, Japanese Society for Synchrotron Radiation Research
2008	The Commendation for Science and Technology by MEXT, Japan Science and Technology Prize (Research Field)
2008	Morita Memorial Prize

Member
Secretary
ISHIKAWA, Azusa

Keywords Condensed Matter, Optical and Photoelectrical Properties, Synchrotron Radiation

Physical and chemical properties of solids, such as conductivity, magnetism, superconductivity and chemical reactions originate from microscopic electronic structure, lattice/molecular vibrations, and molecular movements based on quantum mechanics in materials and their interactions. By revealing the microscopic states, we can learn about the origin of physical and chemical properties and hidden functionalities. Also, the microscopic information is helpful for the creation of novel functional properties. To visualize hidden microscopic information, we develop novel spectroscopic techniques using synchrotron radiation, high brilliant electron beams, and other so-called quantum beams. We are now developing a new electron spectroscopy technique, namely Spin-Resolved resonant Electron-Energy-Loss Spectroscopy (SR-rEELS), with bulk-sensitive primary energies of 0.3–1.5 keV, as shown in Figure 1, in order to detect spin-selective element-specific bulk plasmons. Based on the obtained information of electronic structures, we aim to develop novel physical properties of new materials.

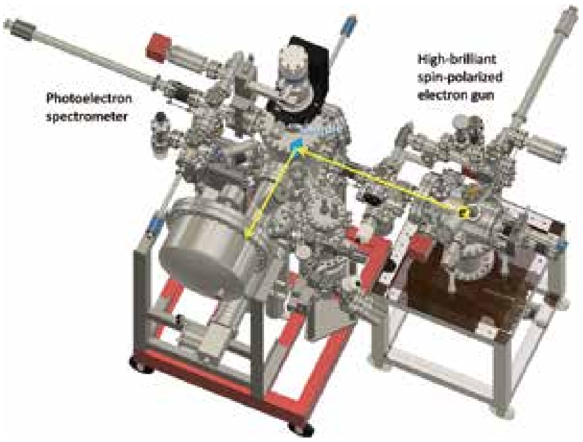

Figure 1. Spin-Resolved resonant Electron-Energy-Loss Spectroscopy (SR-rEELS) apparatus developed by our group. The apparatus consists of a high-brilliant spin-polarized electron gun and a photoelectron spectrometer.

Selected Publications

- Y. Ohtsubo, Y. Yamashita, K. Hagiwara, S. Ideta, K. Tanaka, R. Yukawa, K. Horiba, H. Kumigashira, K. Miyamoto, T. Okuda, W. Hirano, F. Iga and S. Kimura, "Non-Trivial Surface States of Samarium Hexaboride at the (111) Surface," *Nat. Commun.* **10**, 2298 (7 pages) (2019).
- K. Hagiwara, Y. Ohtsubo, M. Matsunami, S. Ideta, K. Tanaka, H. Miyazaki, J. E. Rault, P. Le Fèvre, F. Bertran, A. Taleb-Ibrahimi, R. Yukawa, M. Kobayashi, K. Horiba, H. Kumigashira, K. Sumida, T. Okuda, F. Iga and S. Kimura, "Surface Kondo Effect and Non-Trivial Metallic State of the Kondo Insulator YbB_{12}," *Nat. Commun.* **7**, 12690 (7 pages) (2016).
- S. Kimura and H. Okamura, "Infrared and Terahertz Spectroscopy of Strongly Correlated Electron Systems under Extreme Conditions," *J. Phys. Soc. Jpn.* **82**, 021004 (28 pages) (2013). [review]
- S. Kimura, T. Iizuka, H. Miyazaki, A. Irizawa, Y. Muro and T. Takabatake, "Electronic-Structure-Driven Magnetic Ordering in a Kondo Semiconductor $CeOs_2Al_{10}$," *Phys. Rev. Lett.* **106**, 056404 (4 pages) (2011).

1. Magneto-Optics of the Weyl Semimetal TaAs in the THz and IR Regions[1)]

The magnetic-field dependence of optical conductivity [σ(ω)] spectra of the ideal type-I Weyl semimetal TaAs has been investigated at the temperature of 10 K in the terahertz (THz) and infrared (IR) regions. The obtained σ(ω) spectrum in the THz region of $\hbar\omega \leq 15$ meV is strongly affected by the applied magnetic field (B): The Drude spectral weight is rapidly suppressed, and an energy gap originating from the optical transition in the lowest Landau levels appears with a gap size that increases in proportion to $\sqrt{B}$, which suggests linear band dispersions. The obtained THz σ(ω) spectra could be scaled not only in the energy scale by $\sqrt{B}$ but also in the intensity by $1/\sqrt{B}$ as shown in Figure 2, which has been predicted theoretically. In the IR region for $\hbar\omega \geq 17$ meV, on the other hand, the observed $R(\omega)$ peaks originating from the optical transitions in higher Landau levels are proportional to linear-B suggesting parabolic bands. The different band dispersions suggests that the Dirac linear bands transient to the free-electron-like parabolic bands with increasing energy.

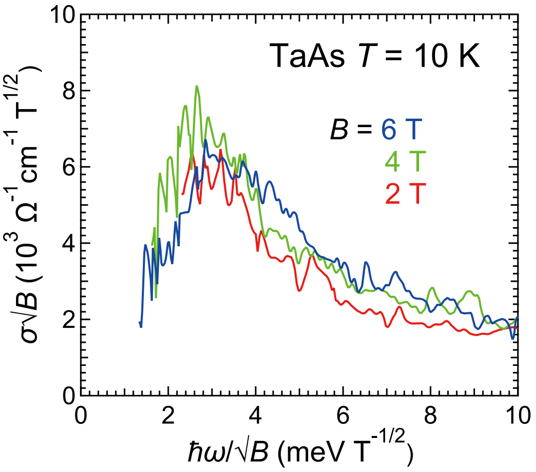

Figure 2. Magnetic-field dependence of optical conductivity [σ(ω, B)] spectrum of TaAs in the THz region at the temperature of 10 K. The horizontal and vertical axes are normalized by B and $1/\sqrt{B}$, respectively.

2. One-Dimensionality of the Spin-Polarized Surface Conduction and Valence Bands of Quasi-One-Dimensional Bi Chains on GaSb(110)-(2×1)[2)]

Surface electronic structure and its one-dimensionality above and below the Fermi level (E_F) are surveyed on the Bi/GaSb(110)-(2×1) surface hosting quasi-one-dimensional (Q1D) Bi chains, using conventional (one-photon) and two-photon angle-resolved photoelectron spectroscopy (ARPES) and theoretical calculations. ARPES results reveal that the Q1D electronic states are within the projected bulk band gap. Circular dichroism of two-photon ARPES and density-functional-theory calculation indicate clear spin and orbital polarization of the surface states consistent with the giant sizes of Rashba-type spin–orbit interaction (SOI), derived from the strong contribution of heavy Bi atoms. The surface conduction band above E_F forms a nearly straight constant-energy contour (Figure 3a), suggesting its suitability for application in further studies of one-dimensional electronic systems with strong SOI. A tight-binding model calculation based on the obtained surface electronic structure successfully reproduces the surface band dispersions (Figures 3b, 3c) and predicts possible one- to two-dimensional crossover in the temperature range of 60–100 K.

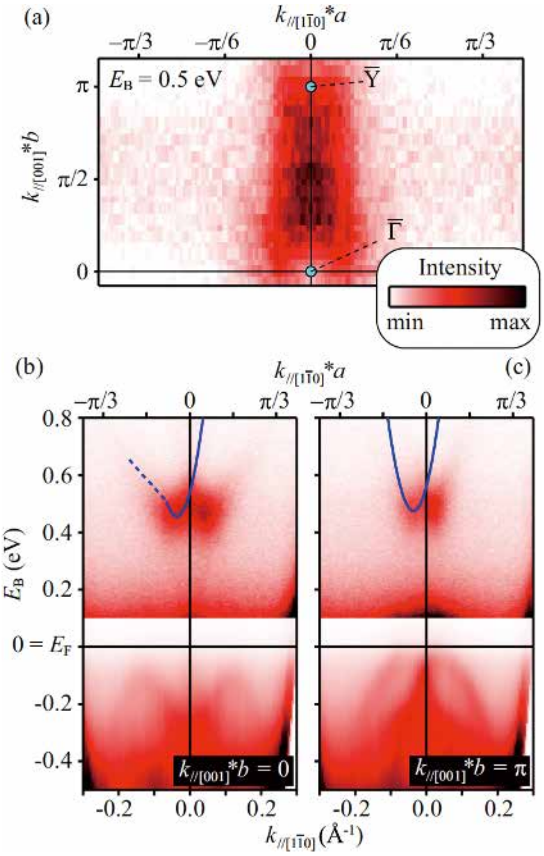

Figure 3. ARPES intensity plots of Bi/GaSb(110)-(2×1) at 25 K taken with two laser pulses. A delay time between the pump and probe pulses was set to 1 ps. The pump pulses ($h\nu$ = 1.5 eV) were linearly polarized photons, the electric field vector, which lies in the photon incident plane. The probe ones had the same incident plane as the circular polarization ($h\nu$ = 6.0 eV). (a) Constant energy contour at E_B ~ 0.5 eV. (b) ARPES intensity plot along $\bar{\Gamma}$–$\bar{X}$. The photoelectron signals in $E_B > 0.1$ eV are enhanced to make the surface conduction band dispersion visible. (c) Same as (b) but taken along $\bar{Y}$–$\bar{M}$. Solid and dashed curves in (b) and (c) guide the theoretical band dispersions.

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2) Y. Ohtsubo, N. Tokumasu, H. Watanabe, T. Nakamura, P. Le Fèvre, F. Bertran, M. Imamura, I. Yamamoto, J. Azuma, K. Takahashi and S. Kimura, *Phys. Rev. B* **101**, 235306 (8 pages) (2020).

Innovative Catalysis Development Based on Radiant Light Spectroscopy

Division of Advanced Molecular Science (Department of Photo-Molecular Science, Photo-Molecular Science III)

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Education

1993	B.S. Osaka University
1995	M.S. Osaka University
1998	Ph.D. Osaka University

Professional Employment

1995	JSPS Research Fellow
1998	Assistant Professor, Osaka University
2002	Guest Scientist, Scripps Research
2008	Associate Professor, Kyoto University
2019	Associate Professor (Cross Appointment), Institute for Molecular Science

Awards

2001	N.E. CHEMCAT Award in Synthetic Organic Chemistry, Japan
2008	The 22nd Special Young Lecturer in the 88th CSJ Annual Meeting
2012	Theme Chemistry Journal Award
2015	BCSJ Award, The Chemical Society of Japan
2019	BCSJ Award, The Chemical Society of Japan

Member
Secretary
HAGIWARA, Hisayo

Keywords Organometallic Catalyst, Peptide-Based Material, X-Ray Spectroscopy

For future sustainable development, we promote research development of advanced catalysts based on element strategy criteria. Non-precious metal such as iron, nickel, cobalt, and cupper catalysts are investigated for synthetic transformation of various organic molecules related to pharmaceutical and photoelectronic materials. To elucidate the precise catalytic properties and mechanism, X-ray absorption spectroscopy (XAS) and various radiant right spectroscopies provided at UVSOR are used, where development of a solution-phase in situ XAS spectroscopic techniques and system will be intensively conducted for the study of homogeneous organometallic catalysts. Multidisciplinary research covered on DFT and XAS spectroscopy is also conducted to achieve an efficient structural determination technique being never accessible by the conventional XAS-based structural analysis. Using these cutting-edge spectroscopic technologies, we aim to promote innovative catalyst research which enable us highly efficient transformation of extremely unreactive organic molecules such as simple aromatic compounds, CO_2, and biomass into valuable functional materials.

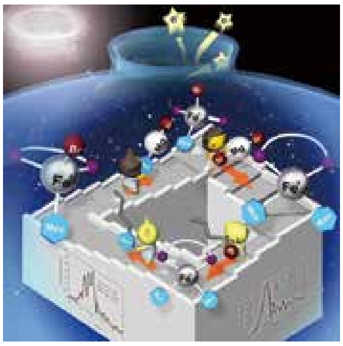


Figure 1. Investigation of iron-catalyzed cross-coupling reactions based on DFT-XAS analysis.

Selected Publications

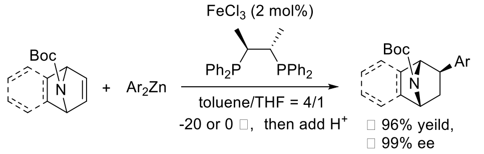
- H. Takaya, S. Nakajima, N. Nakagawa, K. Isozaki, T. Iwamoto, R. Imayoshi, N. Gower, L. Adak, T. Hatakeyama, T. Honma, M. Takagi, Y. Sunada, H. Nagashima, D. Hashizume, O. Takahashi and M. Nakamura, "Investigation of Organoiron Catalysis in Kumada–Tamao–Corriu-Type Cross-Coupling Reaction Assisted by Solution-Phase X-Ray Absorption Spectroscopy," *Bull. Chem. Soc. Jpn.* **88**, 410–418 (2015).
- R. Agata, H. Takaya, T. Iwamoto, T. Hatakeyama, K. Takeuchi, N. Nakatani and M. Nakamura, "Iron-Catalyzed Cross Coupling of Aryl Chlorides with Alkyl Grignard Reagents: Synthetic Scope and Fe^{II}/Fe^{IV} Mechanism Supported by X-Ray Absorption Spectroscopy and Density Functional Theory Calculations," *Bull. Chem. Soc. Jpn.* **92**, 381–390 (2019).
- Y. Kanazawa, T. Mitsudome*, H. Takaya* and M. Hirano*, "Pd/Cu-Catalyzed Dehydrogenative Coupling of Dimethyl Phthalate: Synchrotron Radiation Sheds Light on the Cu Cycle Mechanism," *ACS Catal.* **10**, 5909–5919 (2020).
- L. Adak, M. Jin, S. Saito, T. Kawabata, T. Itoh, S. Ito, A. K. Sharma, N. J. Gower, P. Cogswell, J. Geldsetzer, H. Takaya, K. Isozaki and M. Nakamura*, "Iron-Catalysed Enantioselective Carbometalation of Azabicycloalkenes," *Chem. Commun.* **57**, 6975–6978 (2021).

1. DFT-XAS-based Mechanistic Investigation of Transition-Metal-Catalyzed Reaction in Homogeneous Phase[1–4]

Mechanistic study on transition-metal complex-catalyzed reaction in homogeneous phase mostly carried out by means of solution-phase NMR analysis. However, studies on base metal catalysts being essential for SDGs achievement often suffer from difficulties due to their paramagnetic property which provide unusual large paramagnetic shifts with significant peak broadening. To solve the problems in mechanistic study of base metal-catalyzed reaction, we conducted to use XAS which enables element specific analysis to determine the oxidation state and the geometry of catalytic species without interference from the paramagnetic property.

Recently, we have succeeded to elucidate the mechanism of Pd/Cu-catalyzed oxidative coupling of dimethyl phthalate where the oxidation states and the local coordination geometries of catalytic intermediates were determined under the stoichiometric conditions of each reaction path.[1,2] DFT- and single crystal X-ray structural analysis adequately provided the precise molecular structure of these intermediates. This research is the first to provide a clear answer to the long-term debate on the reaction mechanism in the last three decades and demonstrated that XAS is the powerful tool for the mechanistic study on homogeneous paramagnetic transition-metal complex-catalyzed reactions being difficult by means of the conventional solution-phase NMR analysis.

Effectiveness of the DFT-XAS-based mechanistic study on paramagnetic transition-metal complex-catalyzed reaction was clearly demonstrated in iron-catalyzed enantioselective carbometallation of azabicycloalkenes (eq. 1).[3] In this study, formation of diphosphine ligand-coordinated tetrahedral iron species, which is a key species for chiral recognition of substrate, was successfully identified with the molecular structure in the reaction mixture.



(1)

2. XAFS-Based Structural Study on Flexible Organometallic Systems[5–7]

Generally, organometallics bearing highly flexible molecular structure make it difficult to prepare a single crystal bearing sufficient size and quality for X-ray crystallography. We conducted DFT-XAS-based structural analysis of such flexible molecule. Recently, Prof. Uemura and Benjamin found a flexible MOF prepared from $[Zn_2(BDC)_2(DABCO)]_n$ and polystyrene which has a polymer-threaded multi-layered structure after removing the DABCO pillar ligand. The polymer-threaded extremely flexible molecular scaffolds showed no clear diffraction pattern except for a broad peak. To determine the molecular structure of this flexible MOF system, we carried out Zn K-edge and O K-edge XAS. A DFT-based simulation of both XAS spectra clearly demonstrated that $[Zn_2(BDC)_2]_n$-monolayer was preserved well in the turbostratic phase without DABCO pillar.[4]

Another successful application was achieved in the structure determination of double-decker type iron porpyrin/phtalocyanine dimer in which two units of iron-porpyrin or phtalocyanine were interlocked through highly flexble quadruplet axials or iron-oxo linkage.[5,6] Fe K-edge XAS-based structural analysis supproted with DFT-MD-based simulation succefully provides the precise local coordionation geometry of iron centers in highly flexible supramolecular system.

Another successful example of the DFT-XAS-based structural study was demonstrated by the molecular strucutre detertmination of an anionic homoleptic organo–transition metal complex of $[Li(12\text{-crown-}4)_2][MPh_6\{Li(thf)\}_2]$ (M = Rh and Ir) in THF solution which are the first examples of hexaaryl complexes of d6 metals with a partially contacted ion pair structure of Ir^{2-}-Li^{+} in solution-phase.[7]

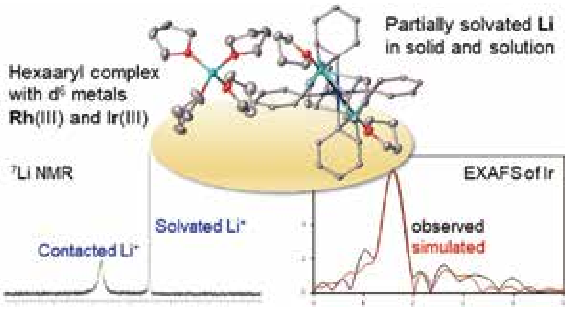


Figure 2. The molecular structure determination of $[Li(12\text{-crown-}4)_2][MPh_6\{Li(thf)\}_2]$.

References

1) H. Masafumi*, K. Sano, Y. Kanazawa, N. Komine, Z. Maeno, T. Mitsudome and H. Takaya*, *ACS Catl.* **8**, 5827–5841 (2018).
2) Y. Kanazawa, T. Mitsudome*, H. Takaya* and M. Hirano*, *ACS Catal.* **10**, 5909–5919 (2020).
3) L. Adak, M. Jin, S. Saito, T. Kawabata, T. Itoh, S. Ito, A. K. Sharma, N. J. Gower, P. Cogswell, J. Geldsetzer, H. Takaya, K. Isozaki and M. Nakamura*, *Chem. Commun.* **57**, 6975–6978 (2021).
4) L. O. Benjamin, H. Takaya and T. Uemura*, *J. Am. Chem. Soc.* **141**, 14549–14553 (2019).
5) Y. Yamada*, K. Morita, T. Sugiura, Y. Toyoda, N. Mihara, M. Nagasaka, H. Takaya, K. Tanaka, T. Koitaya, N. Nakatani, H. Ariga-Miwa, S. Takakusagi, Y. Hitomi, T. Kudo, Y. Tsuji, K. Yoshizawa and K. Tanaka*, *ChemRxiv* DOI: 10.26434/chemrxiv.14728860.v1 (2021).
6) N. Mihara, Y. Yamada*, H. Takaya, Y. Kitagawa, K. Igawa, K. Tomooka, H. Fujii and K. Tanaka*, *Chem. –Eur. J.* **25**, 3369–3375 (2019).
7) T. Iwasaki*, Y. Hirooka, H. Takaya, T. Honma and K. Nozaki*, *Organometallics* **40**, 2489–2495 (2021).

RESEARCH ACTIVITIES

Division of Research Innovation and Collaboration

As the open innovation hub managed by IMS and companies, we conduct the research projects in collaboration with Academia, Industry and Government.

Micro Solid-State Photonics

Division of Research Innovation and Collaboration

TAIRA, Takunori
Project Professor
[taira@ims.ac.jp]

Education

1983	B.A. Fukui University
1985	M.S. Fukui University
1996	Ph.D. Tohoku University

Professional Employment

1985	Researcher, Mitsubishi Electric Corp.
1989	Research Associate, Fukui University
1993	Visiting Researcher, Stanford University (–1994)
1998	Associate Professor, Institute for Molecular Science Associate Professor, The Graduate University for Advanced Studies
2018	Group Director, RIKEN SPring-8 Center
2019	Project Professor, Institute for Molecular Science

Awards

2004	Persons of Scientific and Technological Research Merits, Commendation by Minister of Education, Culture, Sports, Science and Technology, Japan
2010	OSA Fellow Award, The Optical Society (OSA)
2012	SPIE Fellow Award, The International Society for Optical Engineering (SPIE)
2014	IEEE Fellow Award, The Institute of Electrical and Electronics Engineers (IEEE)
2018	IAPLE (The International Academy of Photonics and Laser Engineering) Fellow
2019	LSJ (The Laser Society of Japan) Fellow

Member
Program Manager
SANO, Yuji
Visiting Professor
KAWASE, Kodo
Visiting Associate Professor
YOSHIDA, Mitsuhiro
Post-Doctoral Fellow
TAKEYA, Kei
ISHIZUKI, Hideki
SATO, Yoichi
YAHIA, Vincent
LIM, Hwanhong
TSUJI, Akihiro
Research Fellow
KAUSAS, Arvydas
Technical Fellow
MATSUDA, Miho
KOBAYASHI, Jun
MIZUSHIMA, Kazuhiko
Secretary
ONO, Yoko
INAGAKI, Yayoi

Keywords Solid-State Lasers, Nonlinear Optics, Micro Solid-State Photonics

"Micro Solid-State Photonics" based on the micro domain structure and boundary controlled materials, opens new horizon in the laser science. The engineered materials of micro and/or microchip solid-state, ceramic and single-crystal, lasers can provide excellent spatial mode quality and narrow linewidths with enough power. High-brightness nature of these lasers has allowed efficient wavelength extension by nonlinear frequency conversion: The world first laser ignited car, highly efficiency broad frequency conversions from the wavelength of 118nm VUV until 300–500µm THz waves, and so on. In addition, the quasi phase matching (QPM) is an attractive technique for compensating phase velocity dispersion in frequency conversion. Lately, we propose a new architecture to realize a monolithic multi-disk laser by the surface activated bonding (SAB). This multiple thin-disk or chip gain medium for distributed face cooling (DFC) structure can manage the high-power and high-field laser with high-gain compact system. Besides, QPM-structured crystal quartz constructed by multi-plate stacking could be promising as a high-power and reliable VUV frequency conversion devices. These downsized and modularized **tiny integrated lasers** (TILA) promise the extremely high-brightness lasers to open up the new science, such as laser driven electron accelerator toward table-top XFEL, and innovation by the compact power laser (Figure 1).

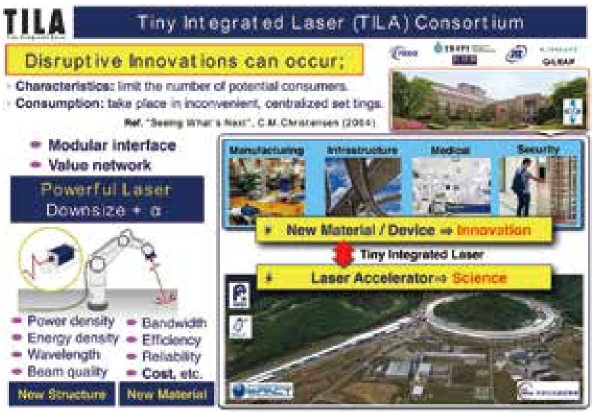


Figure 1. TILA consortium toward "Laser Science and Innovation" by micro solid-state photonics.

Selected Publications

- T. Taira *et al.*, *Opt. Lett.* **16**, 1955 (1991).
- T. Taira *et al.*, *IEEE J. Sel. Top. Quantum Electron.* **3**, 100 (1997).
- T. Taira, *IEEE J. Sel. Top. Quantum Electron.* **13**, 798 (2007).
- T. Taira, *Opt. Mater. Express* **1**, 1040 (2011).
- Y. Sato *et al.*, *Sci. Rep.* **7**, 10732 (2017).
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- T. Taira *et al.*, *The 1st Laser Ignition Conference '13, OPIC '13, Yokohama, April 23-26*, LIC3-1 (2013).
- R. Bhandari *et al.*, *Opt. Express* **21**, 28849 (2013).
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- L. Zheng *et al.*, *Opt. Mater. Express* **7**, 3214 (2017).
- H. Ishizuki *et al.*, *Opt. Mater. Express* **8**, 1259 (2018).
- N. H. Matlis *et al.*, *Nucl. Instrum. Methods Phys. Res., Sect. A* **909**, 27 (2018).
- S.W. Jolly *et al.*, *Nat. Commun.* **10**, 1 (2019).

1. Radiation Dose Rate Effects on the Properties of a Laser-Induced Breakdown Spectroscopy System Developed Using a Ceramics Micro-Laser for Fiber-Optic Remote Analysis[1)]

Radiation dose rate effects on the properties of a compact fiber-optic laser-induced breakdown spectroscopy (LIBS) system with a monolithic Nd:YAG/Cr:YAG composite ceramics were investigated for remote analysis in a hazardous environment. To investigate radiation effects on the LIBS signal, properties related to the Nd:YAG laser operation such as oscillation threshold, output energy, oscillation timing, temporal pulse shape, and beam profile was measured as a function of the radiation dose rate from 0 to 10 kGy/hr in view of their influences to the signal (Figure 2). LIBS spectra of zirconium metal were measured under irradiation. Although signal intensity decreased considerably by irradiation, informative spectra were well obtained even at the maximum radiation dose rate. From the comparison of the LIBS-related parameters among the laser properties, the signal reduction was mainly ascribed to the pulse energy reduction. Scintillation emission spectra were also measured from the ceramics during the irradiation, where the signal intensity increased linearly with the dose rate. The results show that the developed system is applicable to effective remote elemental analysis and monitoring of radiation dose rate in hazardous environments such as nuclear fuel debris inspection.

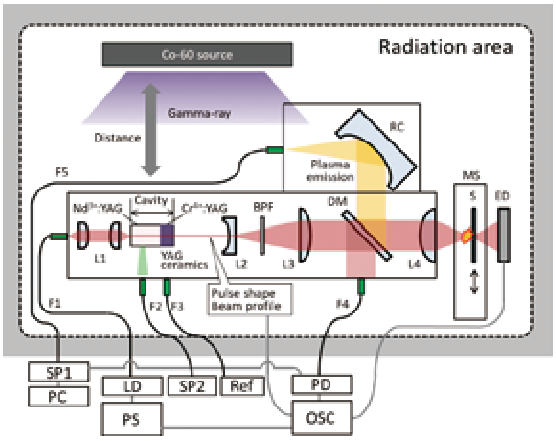


Figure 2. Experimental setup to study the properties of the FO-MC LIBS system in radiation environment.

2. Deformation Properties of Laser Peen Forming Using Sub-Nanosecond Microchip Laser[2)]

A high-power pulsed microchip laser, which has a pulse duration of sub-nanosecond order, had been developed. A focused microchip laser pulse can induce an effective shock wave for deforming the irradiated metal surface plastically. When a sheet metal is scanned by the laser, dieless sheet forming, called laser peen forming, is achieved through the accumulation of such plastic deformations. The authors have applied the method to sheet metal bending (Figure 3). A tamping layer, such as water, on a target surface encourages laser-induced shock waves. Therefore, the sheet metals were irradiated in water. Several materials were bent, and the feasibility of the process was confirmed. Fundamental deformation properties in teams of forming parameters, such as defocusing, pulse energy, material hardness, and thickness, were examined. It was confirmed that, qualitatively, the process had similar deformation modes to those obtained by peen forming. However, when fluence was greatly increased by focusing the pulse energy, laser absorption by water reduced the bending deformation.

Figure 3. Example of bend workpiece (A1100, *t* = 1 mm).

3. Study on the Specific Heat of $Y_3Al_5O_{12}$ between 129 K and 573 K[3)]

We measured the isopiestic specific heat (C_P) of $Y_3Al_5O_{12}$ (YAG) by the differential scanning calorimetry aiming to obtain thermal parameters under cryogenic and room-temperature (RT) conditions. It was also found that the applicable temperature range of our numerical model for C_P of YAG was updated to the range between 129 K and 573 K with below 3% error. Obtained parameters were verified by the comparative study with the first principles calculations. Discrepancy between the calculation value and measured value at 273 K was 0.017 J/gK in C_P. Figure 4 also shows the reason why reported ΘD of YAG has been variated from 500 K to 900 K. ΘD shows the dependence to gradually decrease T towards 0 K and to gradually increase ΘD over 800 K, and to gradually increase T over 600 K under the isopiestic condition and to gradually decrease ΘD toward below 500 K.

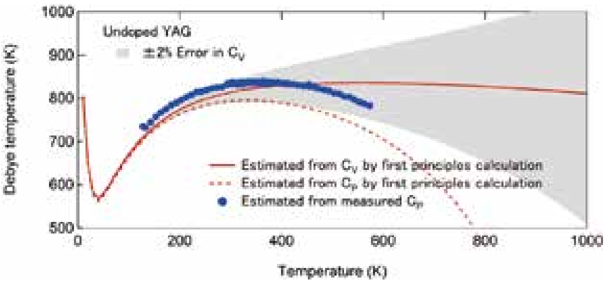


Figure 4. Temperature dependence of ΘD by our model.

References

1) K. Tamura, H. Ohba, M. Saeki, T. Taguchi, H. H. Lim, T. Taira and I. Wakaida, *J. Nucl. Sci. Technol.* **58**, 405 (2020). DOI: 10.1080/00223131.2020.1854880

2) Y. Sagisaka, T. Kawasaki, V. Yahia, T. Taira and Y. Sano, *Journal of the JSTP* **62**, 8 (2021). (in Japanese). DOI: 10.9773/sosei.62.8

3) Y. Sato and T. Taira, *Opt. Mater. Express* **11**, 551 (2021). DOI: 10.1364/OME.416480

RESEARCH FACILITIES

The Institute includes four research facilities, UVSOR Synchrotron Facility, Instrument Center, Equipment Development Center, and Research Center for Computational Science (Okazaki Research Facilities).

UVSOR Synchrotron Facility

KERA, Satoshi	Director, Professor
KATOH, Masahiro	Project Professor
TANAKA, Kiyohisa	Associate Professor
TAIRA, Yoshitaka	Associate Professor
MATSUI, Fumihiko	Senior Researcher
IWAYAMA, Hiroshi	Assistant Professor
OHIGASHI, Takuji	Assistant Professor
IDETA, Shin-ichiro	Assistant Professor
FUJIMOTO, Masaki	Assistant Professor
SUGITA, Kento	Assistant Professor
MATSUDA, Hiroyuki	Post-Doctoral Fellow
SALEHI, Elham	Post-Doctoral Fellow
HAYASHI, Kenji	Engineer (Unit Leader)
NAKAMURA, Eiken	Chief Engineer
MAKITA,Seiji	Engineer
YAMAZAKI, Jun-ichiro	Chief Technician
SAKAI, Masahiro	Chief Technician
YANO, Takayuki	Chief Technician
OKANO, Yasuaki	Chief Technician
TESHIMA, Fumitsuna	Technician
KONDO, Naonori	Technician
YUZAWA, Hayato	Technician
OTA, Hiroshi	Technician
HORIGOME, Toshio	Technical Fellow
MINAKUCHI, Aki	Technical Fellow
MIZUKAWA, Tetsunori	Technical Fellow
ISHIHARA, Mayumi	Secretary
KAMO, Kyoko	Secretary

Outline of the UVSOR Synchrotron Facility

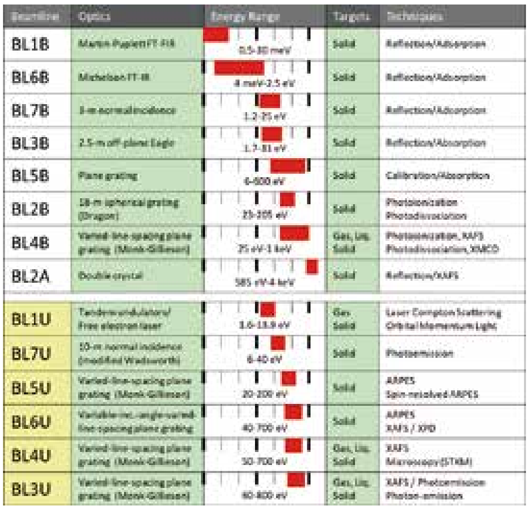
Since the first light in 1983, the UVSOR Synchrotron Facility has been successfully operated as one of the major synchrotron light sources in Japan. After the major upgrade of accelerators in 2003, UVSOR Synchrotron was renamed to UVSOR-II Synchrotron and became one of the world's brightest low energy synchrotron light sources. In 2012, it was upgraded again and has been renamed to be UVSOR-III Synchrotron. The brightness of the electron beam was increased further. Today, six undulators are installed in total, and the storage ring, that is *ca.* 53 meters in circumference, is regularly operated in the top-up mode, irrespective of multi bunches or single bunch.

The UVSOR accelerator complex consists of a 15 MeV injector LINAC, a 0.75 GeV booster synchrotron, and a 0.75 GeV storage ring. The magnet lattice of the storage ring consists of four extended double-bend cells with distributed dispersion function. The single bunch top-up operation (176 ns, 5.6 MHz) for time-resolved measurements or low current measurements is also conducted for two weeks per year.

Six undulators and eight bending magnets provide synchrotron radiation (SR). The bending magnet, its radius of 2.2 m, produces SR with the critical energy of 425 eV. There are eight bending magnet beamlines (Table. 1). Three of the six undulators are in-vacuum soft X-ray (SX) linear-polarized undulators (BL3U, BL4U, and BL6U) and the other three are vacuum/extreme ultraviolet (VUV/XUV or EUV) circular-polarized undulators (BL1U, BL5U, and BL7U). Two beamlines, BL1U and BL6U, are so-called "in-house beamlines," which are dedicated to strategic projects conducted by internal IMS groups in tight collaboration with domestic and foreign scientists. The BL1U can produce pulsed γ-ray radiation by laser Compton scattering technique. In 2021, it was developed by constructing a laser transport system to generate high-intense γ-ray beams. Other twelve beamlines are so-called "public beamlines," which are open to scientists from universities, governmental research institutes, public and private enterprises, and also to overseas scientists. After each development, the in-house beamline will be opened for use as a public beamline.

From the viewpoint of photon energies, we have one SX station equipped with a double-crystal monochromator, seven SX stations with a grazing incidence monochromator, three VUV stations with a normal incidence monochromator, two IR/THz stations equipped with Fourier transform interferometers and one beamline for light source development without any monochromators.

Table 1. List of beamlines at UVSOR-III Synchrotron.



Beamline	Optics	Energy Range	Targets	Techniques
BL1B	Martin-Puplett FT-FIR	0.5-30 meV	Solid	Reflection/Adsorption
BL6B	Michelson FT-IR	4 meV-2.5 eV	Solid	Reflection/Adsorption
BL7B	3-m normal incidence	1.2-25 eV	Solid	Reflection/Adsorption
BL3B	2.5-m off-plane Eagle	1.7-31 eV	Solid	Reflection/Absorption
BL5B	Plane grating	6-600 eV	Solid	Calibration/Absorption
BL2B	18-m spherical grating (Dragon)	23-205 eV	Solid	Photoionization Photodissociation
BL4B	Varied-line-spacing plane grating (Monk-Gillieson)	25 eV-1 keV	Gas, Liq. Solid	Photoionization, XAFS Photodissociation, XMCD
BL2A	Double crystal	585 eV-4 keV	Solid	Reflection/XAFS
BL1U	Tandem undulators/ Free electron laser	1.6-13.9 eV	Gas Solid	Laser Compton Scattering Orbital Momentum Light
BL7U	10-m normal incidence (modified Wadsworth)	6-40 eV	Solid	Photoemission
BL5U	Varied-line-spacing plane grating (Monk-Gillieson)	20-200 eV	Solid	ARPES Spin-resolved ARPES
BL6U	Variable-inc.-angle-varied-line-spacing plane grating	40-700 eV	Solid	ARPES XAFS / XPD
BL4U	Varied-line-spacing plane grating (Monk-Gillieson)	50-700 eV	Gas, Liq. Solid	XAFS Microscopy(STXM)
BL3U	Varied-line-spacing plane grating (Monk-Gillieson)	60-800 eV	Gas, Liq. Solid	XAFS / Photoemission Photon-emission

Inter-University and International Collaboration Programs

A variety of molecular science and related subjects have been carried out at UVSOR Synchrotron Facility by IMS and external/overseas researchers. The cumulative total number of visiting researchers (person-days) per year tops > 4000, who come from > 60 different institutes. International collaborations are also pursued actively, and the number of visiting foreign researchers reaches ~70. UVSOR-III Synchrotron invites new/continuing research proposals twice a year. The proposals both for academic and public research (charge-free) and for private enterprises (charged) are acceptable. COVID-19 issue has a serious impact on user activity, the overseas activity was almost dropped especially. The fruits of the research activities using UVSOR-III Synchrotron are published as the UVSOR ACTIVITY REPORT annually.

Recent Developments

The UVSOR accelerators have been operated for 38 years. We have been upgrading and replacing the machine components, such as magnet power supplies or RF power amplifiers, to continue the stable operation. In these years, troubles occurred on some core components, such as the vacuum chambers and the magnets. We are carefully planning their replacements with short shutdown periods and under the limitation of the facility budget.

On the other hand, we are also putting effort into setting up state-of-the-art experimental stations that takes advantage of our unique beamline performance. BL5U is an angle-resolved photoemission spectroscopy (ARPES) beamline with micro-focused beam (23×40 µm). By combining the latest version of ARPES analyzer (MB Scientific AB, A-1 analyzer Lens#5) with the super quick deflector scan mode, users can perform ARPES measurements on small samples or inhomogeneous samples without changing the sample position. In 2020, a new spin-resolved ARPES system with multi-channel detection (we call "image-spin" detection) has been installed. As shown in Figure 1, we successfully obtained spin-resolved ARPES image of Rashba spin splitting in Au(111) surface states, which was taken at once. According to the rough estimation, the efficiency is 100 times better and the momentum resolution is several times better than the current synchrotron-based ARPES with single-channel detection in the world.

UVSOR has several ARPES beamlines and users can choose proper beamline according to their purpose. At BL7U, high-energy resolution ARPES is available with extremely low energy of photons (6 eV~) using low-temperature 6-axis manipulator (4 K~). In BL6U, photoelectron momentum microscope (PMM), which is an electronic spectroscopy with both the real space and momentum space resolution, has been installed in February 2020 (SPECS Surface Nano Analysis GmbH, KREIOS 150 MM).[1] It will be upgraded to a double hemispherical analyzer in FY2021 and will have spin-resolved function in the future.

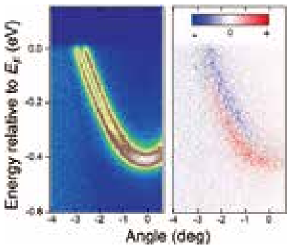


Figure 1. Rashba spin splitting in Au(111) surface states (left) and spin-resolved ARPES image showing the spin polarization (right).

Research Highlights

One of the highlights of the UVSOR research activities this year is the discovery of an ultrathin liquid cell for X-ray absorption spectroscopy (XAS) in the low-energy region at BL3U. Recently, we have investigated local structures of several aqueous solutions and various chemical processes in solution such as catalytic and electrochemical reactions and laminar flows in microfluidics by using *operando* XAS in C, N, and O K-edges.[2,3] On the other hand, the low-energy region below 200 eV is important for chemical research since it includes K-edges of Li and B and L-edges of Si, P, S, and Cl. BL3U has an advantage to measure XAS in the low-energy region with a high photon flux. Recently, we have established an argon gas window that is effective from 60 to 240 eV with the removal of high order X-rays.[4] The SX transmission calculation proposed that XAS in the low-energy region needs an ultrathin liquid cell with the 2.6 mm optical length of Ar gas.

Figure 2 shows the XAS measurement system including the ultrathin liquid cell. The ultrathin liquid cell is in an atmospheric Ar condition and is separated from the beamline and a photodiode detector under ultrahigh vacuum conditions with Si_3N_4 membranes (0.2 × 0.2 mm^2). The 2.6 mm optical length of argon gas has been realized owing to the ultrathin liquid cell. XAS spectra of 2 M LiCl solutions at Li K-edge and Cl L-edge were successfully obtained by using this liquid cell. In the future, XAS in the low-energy region will be applied to various chemical processes in solution, such as a Li-ion battery, Ni-borate electrocatalysts, and organic reactions with organosilicons, organolithiums, and organoboranes.

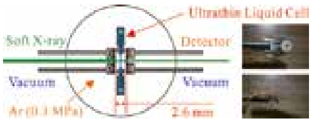


Figure 2. A schematic of the XAS measurement system in the low-energy region including the ultrathin liquid cell. Photographs of the ultrathin liquid cell are also shown.

References

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2) M. Nagasaka *et al.*, *Anal. Sci.* **36**, 95 (2020).
3) M. Nagasaka and N. Kosugi, *Chem. Lett.* **50**, 956 (2021).
4) M. Nagasaka, *J. Synchrotron Radiat.* **27**, 959 (2020).

Awards

NAKAMURA, Eiken; The Chemical Society of Japan Award for Technical Achievements for 2020 (2021).
NAKAMURA, Eiken; The Commendation for Science and Technology by the Minister of Education, Culture, Sports, Science and Technology Outstanding Support for Research Award (2021).

Instrument Center

YOKOYAMA, Toshihiko	Director, Professor
SUZUKI, Toshiyasu	Team Leader
NAKAMURA, Toshikazu	Team Leader
MINATO, Taketoshi	Senior Researcher
MAKITA, Seiji	Engineer
TAKAYAMA, Takashi	Engineer
FUJIWARA, Motoyasu	Chief Technician
OKANO, Yoshinori	Technician
MIZUKAWA, Tetsunori	Technician
UEDA, Tadashi	Technician
ASADA, Mizue	Technician
URUICHI, Mikio	Technician
MIYAJIMA, Mizuki	Technician
OHARA, Mika	Project Manager
ISHIYAMA, Osamu	Project Manager
HASEGAWA, Hisashi	Project Manager
NAKAMOTO, Keiichi	Project Manager
IKI, Shinako	Technical Fellow
NAGAO, Haruyo	Technical Fellow
FUJIKAWA, Kiyoe	Technical Fellow
TOYAMA, Aya	Technical Fellow
FUNAKI, Yumiko	Secretary
HYODO, Yumiko	Secretary
TOYAMA, Yu	Secretary
ISHIKAWA, Azusa	Secretary
UCHIDA, Mariko	Secretary

Instrument Center was organized in April of 2007 by integrating the general-purpose and state-of-the-art facilities of Research Center for Molecular Scale Nanoscience and Laser Research Center for Molecular Science. The mission of Instrument Center is to support the in-house and external researchers in the field of molecular science, who intend to conduct their researches by utilizing general-purpose and state-of-the-art instruments. The staffs of Instrument Center maintain the best conditions of the machines, and provide consultation for how to use them. The main instruments the Center now maintains in Yamate campus are: Nuclear magnetic resonance (NMR) spectrometers (JNM-ECA 600 for solutions, JNM-ECS400 for solutions and Bruker AVANCE800 Cryoprobe for solutions), matrix assisted laser desorption/ionization time-of-flight (MALDI TOF) mass spectrometer (microflex LRF, Bruker Daltonics), powder X-ray diffractometer (Rigaku RINT-Ultima III), circular dichroism (CD) spectrometer (JASCO JW-720WI), differential scanning calorimeter (MicroCal VP-DSC), isothermal titration calorimeter (MicroCal iTC200), solid-state calorimeter (Rigaku DSC8231/TG-DTA8122), scanning electron microscope (SEM; JEOL JEM-6700F) and elemental analyzer (J-Science Lab Micro Corder JM10). In the Myodaiji campus, the following instruments are installed: Electron spin resonance (ESR) spectrometers (Bruker E680, E500, EMX Plus, ns pulsed laser for time resolved experiments), NMR spectrometer (Bruker AVANCE600 for solids), superconducting quantum interference devices (SQUID; Quantum Design MPMS-7 and MPMS-XL7), solution X-ray diffractometer (Rigaku NANO-Viewer), single-crystal X-ray diffractometers (Rigaku Mercury CCD-1, CCD-2, RAXIS IV, and Rigaku HyPix-AFC), molecular structure analysis using crystalline sponge method (Rigaku XtaLAB P200/PILATUS 200K, Rigaku SuperNova), operando multipurpose x-ray diffraction for powder and thin films (Panalytical Empyrean), thermal analysis instruments (Rigaku DSC8231/TG-DTA8122), fluorescence spectrometer (SPEX Fluorolog), X-ray fluorescence spectrometer (JEOL JSX-3400RII), UV-VIS-NIR spectrometer (Shimadzu UV-3600Plus), Raman microscope (Renishaw INVIA REFLEX 532), picosecond tunable laser system (Spectra Physics Tsunami/Quantronix Titan/Light Conversion TOPAS), low vacuum analytical SEM (Hitachi SU6600), angle resolved ultraviolet photoelectron spectroscopy (ARUPS) for functional band structures (VG-Scienta DA30), and FTIR spectrometer (Bruker IFS 66v/S). Recently, new equipment of high-performance *operando* scanning probe microscopes (Bruker Dimension XR Icon Nanoelectrical and Nanoelectrochemical, two sets) was just installed, and electron spectrometers for chemical analysis (ESCA) equipment (Scienta, R4000L1) was newly registered for public usage in Instrument Center. In the fiscal year of 2020, Instrument Center accepted 85 applications from outside and the total user time amounted 1,871 days for outside and 2,056 days for in-house with 26 equipments. Instrument Center also maintains helium liquefiers in the both campus and provides liquid helium to users (43,818 L/year). Liquid nitrogen is also provided as general coolants used in many laboratories in the Institute (30,455 L/year). Instrument Center also organizes the Inter-University Network for Common Utilization of Research Equipments and the Molecule and Material Synthesis Platform in the Nanotechnology Platform Program supported by Ministry of Education, Culture, Sports, Science and Technology. These special programs are described in the other chapter of the booklet.

Equipment Development Center

YAMAMOTO, Hiroshi	Director
KONDO, Takuhiko	Chief Engineer (Unit Leader)
TOYODA, Tomonori	Engineer
MATSUO, Junichi	Chief Technician
TAKADA, Noriko	Technician
KIMURA, Sachiyo	Technician
KIKUCHI, Takuro	Technician
KIMURA, Kazunori	Technician
SAWADA, Toshihiro	Technical Fellow
YOSHIDA, Hisashi	Technical Fellow
ISHIKAWA, Akiko	Technical Fellow
MIZUTANI, Nobuo	Technical Fellow
SUGANUMA ,Kouji	Technical Fellow
INAGAKI, Itsuko	Secretary

Research and development of novel instruments demanded in the forefront of molecular science, including their design and fabrication, are the missions of this center. Technical staffs in the three work sections, mechanics, electronics and lithography are engaged in developing state-of-the-art experimental instruments in collaboration with scientists. We expanded our service to other universities and research institutes since 2005, to contribute to the molecular science community and to improve the technology level of the center staffs. A few selected examples of our recent developments are described below.

PDMS Mixing Chamber for Soft X-Ray Absorption Spectroscopy

We have fabricated a microfluidic device with flow paths for solution mixing, which is used for soft X-ray absorption spectroscopy. This flow device is equipped with two inclined channel paths which guide liquids to a mixing chamber in addition to a channel for outcoming flow. Width and depth of the flow paths are both 50 μm, and the pattern seen from above is Y-shaped. The diameters of the channels are 0.2 mm, and the bottom of the device is made of SiN membrane. We have produced these flow paths by casting PDMS (polydimethylsiloxane) into a mold. We have made the inclined channel paths by embedding three piano wires with a diameter of 0.2 mm before curing PDMS moiety (Figure 1). We have fixed these wires by using a guide produced by 3D printer. Since some issues have been found in the experiment, we are planning to improve this device.

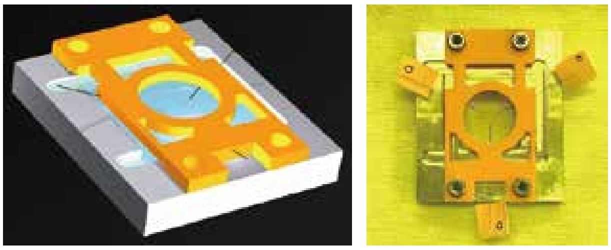


Figure 1. A 3D drawing (left) and picture (right) of the PDMS sample holder in a mold.

Improvement of ECL Logic Circuit with CPLD and Development of an Analog Level Converter

We have developed “a multi-coincidence electronic circuit for time-resolved reaction microscopy of electron Compton scattering” in collaboration with Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, in 2007. The circuit consists of many devices for emitter coupled logic (ECL) to process multiple signals transmitted from position-sensitive-detectors (PSDs).

We have received a request to improve the circuit for higher performance in another experiment. It requires a circuit to accept 13 inputs to be processed into one output signal in Nuclear Instruments Module (NIM) level. Pulse duration of input signals should be stretched using a monostable multivibrator. The output signal is generated by several logical operations. To simplify implementation of such operations, we decided to use CPLD (Complex Programmable Logic Device; XC2C256-7TQ144C by Xilinx) with analog level transducer circuit (Figure 2). All of logical operations are putted into single CPLD and tested by simulation. Level converter circuit that we have developed can convert NIM level pulses into TTL level in a 10 nanoseconds duration time scale (and vice versa) as we expected. We are planning to test them with a virtual system that reproduces the real experimental setup.

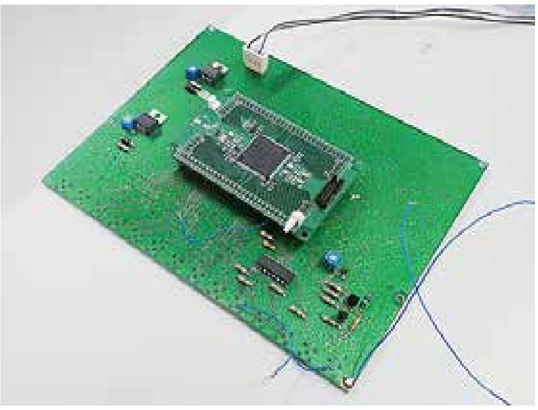
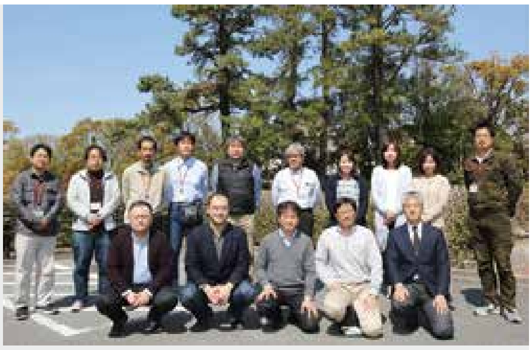


Figure 2. Level conversion circuit and CPLD board assembled for the performance evaluation.

Research Center for Computational Science (Okazaki Research Facilities)

EHARA, Masahiro	Director, Professor
SAITO, Shinji	Professor
OKUMURA, Hisashi	Associate Professor
OKAZAKI, Kei-ichi	Associate Professor
OONO, Hitoshi	Associate Professor
UCHIYAMA, Ikuo	Associate Professor
ISHIDA, Tateki	Assistant Professor
IWAHASHI, Kensuke	Chief Engineer (Unit Leader)
MIZUTANI, Fumiyasu	Engineer
NAITO, Shigeki	Chief Technician
KAMIYA, Motoshi	Chief Technician
SAWA, Masataka	Technician
NAGAYA, Takakazu	Technician
KINOSHITA, Takamasa	Technician
YAZAKI, Toshiko	Technical Fellow
UNO, Akiko	Technical Fellow
KONDO, Naoko	Secretary
KONDO, Noriko	Secretary
URANO, Hiroko	Secretary



Research Center for Computational Science provides state-of-the-art computational resources to academic researchers in molecular science and related fields, *e.g.* solid state physics, biophysics, and physiology. Our systems consist of NEC LX (406Rh-2, 110-Rh1, 108Th-4G; since Oct. 2017). The NEC LX 406Rh-2 and 110-Rh1 combined system, named "Molecular Simulator," is ranked 261st position in the TOP500 supercomputer list in June 2020. These massive computer resources have been used for various kinds of large-scale calculations, for example accurate electronic structure calculations of molecular systems and conformation searches using non-Boltzmann ensemble methods. We also provide a number of application programs to the users: Gaussian, GAMESS, Molpro, AMBER, Gromacs, and so on. The supercomputer systems had been used by 1,142 researchers from 271 groups in fiscal year 2020. Some of the computational resources are provided to the following projects: Program for Promoting Research on the Supercomputer Fugaku, Professional development Consortium for Computational Materials Scientists (PCoMS), and Elementary Strategy Initiative to Form a Core Research Center.

For fostering young generation, we organize the schools of quantum chemistry and molecular dynamics simulation every year. We also organize the RCCS supercomputer workshop focusing on the new trends of computational chemistry for the purpose of the research exchange and human resource development.

We organized a joint Supercomputer workshop of the Research Center for Computational Science and the Nanotechnology Platform Project, "Toward Collaboration between Theoretical/Computational Science and Experimental Science Based on Data Science" and two schools "The 10th Quantum Chemistry School" and "The 14th Molecular Simulation School —From Basics to Applications. In cooperation with Institute for Materials Research, Tohoku University, Institute for Solid State Physics, University of Tokyo, and Nanoscience Design Center, Osaka University, we established the Council for Computational Materials Science to promote the cutting-edge computational materials science technology of Japan, to create world-class results, and to realize the social implementation of simulation technology and materials information science technology.

We also offer Quantum Chemistry Literature Database (QCLDB; http://qcldb2.ims.ac.jp/), Force Constant Database (FCDB; http://fcdb.ims.ac.jp/), and Segmented Gaussian Basis Set (SGBS; http://sapporo.center.ims.ac.jp/sapporo/) services. The latest release, QCLDB II Release 2016, containing 139,657 data of quantum chemical studies is available for the registered users. FCDB provides force constants of molecules collected from literature. SGBS service provides basis sets for atoms which efficiently incorporate valence and core electron correlations (also known as Sapporo basis sets) in various quantum chemistry package formats. Further details about the hardware, software, and the other services are available on our website (English: https://ccportal.ims.ac.jp/en/, Japanese: https://ccportal.ims.ac.jp/).

The center is jointly managed with National Institute for Physiological Sciences and National Institute for Basic Biology (both in the same campus).

Figure 1. NEC LX.

Safety Office

TANAKA, Shoji	Director
TOMURA, Masaaki	Research Assistant
SHIGEMASA, Eiji	Technical Associate
UEDA, Tadashi	Technical Associate
TAKAYAMA, Takashi	Technical Associate
SAKAI, Masahiro	Technical Associate
MAKITA, Seiji	Technical Associate
TESHIMA, Fumitsuna	Technical Associate
KIKUCHI, Takuro	Technical Associate
TSURUTA, Yumiko	Secretary
ASAKURA, Yukiko	Secretary

The Safety Office was established in April 2004. The mission of the Office is to play a principal role in the institute to secure the safety and health of the staffs by achieving a comfortable workplace environment, and improvement of the working conditions. In concrete terms, it carries out planning, work instructions, fact-findings, and other services for safety and health in the institute. The Office is composed of the following staffs: The Director of the Office, Safety-and-Health Administrators, Safety Office Personnel, Operational Chiefs and other staff members appointed by the Director General.

The Safety-and-Health Administrators patrol the laboratories in the institute once every week, and check whether the laboratory condition is kept sufficiently safe and comfortable to conduct researches. The Office also edits the safety manuals and gives safety training courses, for Japanese and foreign researchers.

SUPPORTING STAFF

Research Enhancement Strategy Office

OKAMOTO, Hiromi	Head
YAMAMOTO, Hiroshi	Professor (in charge of Foreign Affairs)
AKIYAMA, Shuji	Professor (in charge of Personnel Affairs)
IINO, Ryota	Professor (in charge of Public Affairs)
ISHIZAKI, Akihito	Professor (in charge of Facilities/Buildings and Foreign Affairs)
KATAYANAGI, Hideki	Research Assistant (in charge of Public Affairs)
SHIGEMASA, Eiji	Technical Associate (in charge of General Affairs)
NAKAMURA, Toshikazu	Team Leader, Instrument Center
FUKUI, Yutaka	URA (Administrative Associate, Assistant to Head)
HARADA, Miyuki	URA (Technical Associate)
KAMETAKA, Ai	URA (Administrative Associate)
NAGASONO, Hisayo	URA (Administrative Associate)
MASE, Toshiaki	Senior Specialist
NAKAMURA, Rie	Technical Fellow
YAZAKI, Toshiko	Technical Fellow
OHTA, Minori	Secretary
KAMIYA, Miho	Secretary
SUZUKI, Satomi	Secretary
SUGIYAMA, Kayoko	Secretary
SHIMODE, Ayako	Secretary
ISHIHARA, Mayumi	Secretary
YOKOTA, Mitsuyo	Secretary

In 2013, Research Enhancement Strategy Office was established in each research institute in NINS by support of the MEXT University Research Enhancement Project of 10 years 2013 to 2023. In this office, university research administrators (URA) and supporting staff members realize several strategic plans for the enhancement of international and inter-university collaborations, public relations, and research activities of young, female, and foreign scientists in collaboration with Head Office in NINS.

Technical and Engineering Department

SHIGEMASA, Eiji	Head of Department
UCHIYAMA, Koichi	Chief Technician
TANAKA, Kei	Secretary

Secretary for Director General

NOGAWA, Kyoko	Secretary

Information Office

TSURUTA, Yumiko	Secretary
ASAKURA, Yukiko	Secretary
KONDO, Naoko	Secretary

All technical staff at IMS belong to the Technical and Engineering Department (TED). IMS offers collaborators a unique array of support services. A group of engineers and technicians technically support not only scientists outside from IMS but also inhouse scientists.

The technical division of IMS (TD-IMS) was initially organized in 1975 as the first organization of technical staff in Japan to support both in-house and outside scientists technically. Over time, the number of personnel with high levels of technical skills in TD-IMS increased dramatically, and the division outgrew its organization system. Consequently, the TD-IMS has been reorganized as the “Technical and Engineering Department” since April 1st 2021.

The TED operates directly under the director general of IMS, and consists of four Units (Optical Engineering Unit, Computing and Information Technology Unit, Equipment Development Unit, and Instrumental Analysis Unit), as well as staff members taking charge of safety, facilities, and publicity activities. Each unit has a unit leader, who manages the unit staff.

In addition, several members belonging to the TED support administrative activities in IMS by managing the Safety Office, the Public Affairs Office, the Archives, and the Information Office.

The annual meeting for technical staff of research institutes and universities in Japan, was organized in 1975 and since then it has been regularly held every year. We aim toward higher technology and knowledge exchange concerning various technical subjects related to our technology and engineering. Our best endeavors have been, and will be made, to promote the advanced research of IMS.

Special Research Projects

IMS has special research projects supported by national funds. Three projects in progress are:

(a) MEXT Nanotechnology Platform Program
Platform of Molecule and Material Synthesis
(b) Inter-University Network for Efficient Utilization of Research Equipments
(c) MEXT Program Advanced Research Infrastructure for Materials and Nanotechnology in Japan:
Spoke Organization in Advanced Material Circulation Techniques

These three projects are being carried out with close collaboration between research divisions and facilities. Collaborations from outside also make important contributions. Research fellows join these projects.

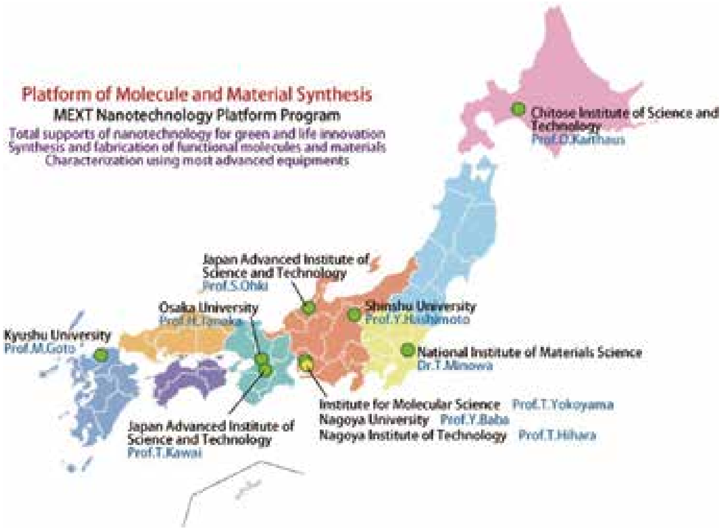
(a) MEXT Nanotechnology Platform Program
Platform of Molecule and Material Synthesis

Since July 2012, Nanotechnology Platform Program supported by Ministry of Education, Culture, Sports, Science and Technology (MEXT) has been conducted in order to promote public usage of various nanotechnology facilities. This program will continue until March 2022 and consists of three platforms of nanostructure analysis, nanoprocessing, and molecule and material synthesis, together with the management center of the platforms. Each platform consists of about ten organizations all over Japan. IMS conducts a representative core organization of the Molecule and Material Synthesis Platform. All the organizations in this platform are shown in Figure. In this platform, to promote green and life innovation researches using nanotechnology related techniques not only for universities and government institutes but also for private companies, we will open various kinds of our facilities with total supports including molecular synthesis, materials fabrications, characterization, data analysis and scientific discussion. We will encourage applications not only to each element, but to combined usage of several supporting elements for biotechnology and green chemistry. In IMS, the number of accepted proposals in FY2020 amounted 128 (111 non-proprietary and 10 proprietary proposals, excluding inhouse applications from IMS) and the total number of days used for the supports is 2127 (1960 days for non-proprietary proposals and 50 days for proprietary ones).

List of Supports in IMS (FY2020)

Supporting Element		Responsible Persons	Charging Persons
Platform Management		T. Yokoyama	M. Ohara, Y. Toyama
Organization Management in IMS			Y. Hyodo, Y. Funaki
UVSOR Synchrotron Radiation	X-Ray Magnetic Circular Dichroism	T. Yokoyama	T. Koitaya, K. Yamamoto, O. Ishiyama
Microstructure Fabrication	Maskless Lithography with Step Gauge	H. Yamamoto	M. Aoyama, T. Kondo, N. Takada, S. Kimura, T. Kikuchi, N. Mizutani, A. Ishikawa
	3D Optical Surface Profiler		
Equipment Development	Machine Shop		M. Aoyama, T. Kondo, T. Toyota, J. Mathuo
Electron Microscopy	Field Emission Scanning Electron Microscopy	T. Yokoyama	O. Ishiyama, A. Toyama
	Low Vacuum Analytical Scanning Electron Microscopy		
	Field Emission Transmission Electron Microscope		S. Iki, T. Ueda, M. Uruichi
X-rays	Single Crystal X-Ray Diffractometer		Y. Okano
	Low Temperature Single Crystal X-Ray Diffractometer for Microcrystals		
	Molecular Structure Analysis using Crystalline Sponge Method		M. Fujita, T. Mitsuhashi
	Powder X-Ray Diffractometer		M. Fujiwara
	Operando Multi-Purpose X-Ray Diffraction		G. Kobayashi, F. Takeiri, M. Fujiwara
	Small Angle X-Ray Scattering for Solutions	S. Akiyama	A. Mukaiyama
Electron Spectroscopy	Angle Resolved Ultraviolet Photoelectron Spectroscopy for Functional Band Structures	S. Kera, K. Tanaka	S. Ideta

Electron Spin Resonance	Pulsed High Field ESR	T. Yokoyama, T. Nakamura	M. Asada, M. Fujiwara, S. Iki, T. Ueda
	X-Band CW ESR		
	X, Q-Band CW ESR		
SQUID	Superconducting Quantum Interference Device		M. Asada, M. Fujiwara, S. Iki
Thermal Analysis	Differential Scanning Calorimeter (Solutions)	T. Yokoyama	T. Mizukawa, M. Uruichi, H. Nagao
	Isothermal Titration Calorimeter (Solutions)		
	Calorimeter for solids		M. Fujiwara
Mass Spectrometer	Matrix Assisted Laser Desorption/Ionization Time of Flight Mass Spectrometer		T. Mizukawa, M. Uruichi, K. Fujikawa
Spectroscopy	Microscopic Raman Spectroscopy		M. Uruichi
	Fourier Transform Far Infrared Spectroscopy		
	Fluorescence Spectroscopy		T. Ueda
	Ultraviolet & Visible Absorption Spectroscopy		
	Circular Dichroism		T. Mizukawa, M. Uruichi, K. Fujikawa
Lasers	Picosecond Laser		T. Ueda
High Field NMR	800 MHz Solutions, Cryostat Probe	K. Kato	M. Yagi, S. Yanaka, Y. Isono
	600 MHz Solids	K. Nishimura	
	600 MHz Solutions	T. Yokoyama	T. Mizukawa, M. Uruichi, H. Nagao
Functional Molecular Synthesis and Molecular Device Fabrication	Organic Thin Film Solar Cells	M. Hiramoto	S. Izawa
	Organic Field Effect Transistors	H. Yamamoto	D. Hirobe
	Functional Organic Synthesis	N. Momiyama, T. Suzuki	N. Ohtsuka, T. Fujinami
	Large Scale Quantum Mechanical Calculations	M. Ehara	
	Magnetic Thin Films	T. Yokoyama	T. Koitaya, K.Yamamoto
	Metal Complexes	T. Kusamoto	R. Matsuoka
	Inorganic Materials	G. Kobayashi	F. Takeiri
	Biomolecule System	S. Akiyama	A. Mukaiyama, Y. Furuike
	Supplementary Apparatus in Instrument Center	T. Yokoyama	



(b) Inter-University Network for Common Utilization of Research Equipments

It is highly important to improve instrumental supporting environments for research and education in the field of science and engineering. Nowadays, advanced research instruments are indispensable for conducting researches and educations with high standard quality. To install such sophisticated instruments, tremendous amount of budgets would be necessary. In 2007, for constructing a national-wide network to provide easy accesses to high-level equipments to researchers and students in universities all over Japan, the five-year project "Functioning of Inter-University Network for Efficient Utilization of Chemical Research Equipments" was launched. The network maintains an internet machine-time reservation and charging system by the help of equipment managers and accounting sections in each university. 72 national universities as well as Institute for Molecular Science (total 73 organizations) all over Japan have been participating in the network. They are grouped into 12 local regions and in each region the regional committee discusses and determines the operation of regional network systems with the hub university chairing. There is no barrier for every user to access to any universities beyond his/her regional group. From 2009, the registered equipments are open to the researchers and students of all the public (prefectural *etc.*) and private universities. Since 2010, the project has been renamed "Inter-University Network for Common Utilization of Research Equipments" still keeping the original strategy and stable functioning. Since 2018, the institutions that provide research facilities are open to public and private universities. Currently, the network is organized by 78 organizations. The number of registered users amounts to 15,000 in 500 universities/institutions/companies covering over 4,000 laboratories in Japan (July, 2021). Network usage reaches about 150,000 times a year, and the number continues to grow. Moreover, we have actively provided various opportunities where technical staffs and users can improve their technical skills and frankly communicate with each other.

(c) MEXT Program Advanced Research Infrastructure for Materials and Nanotechnology in Japan: Spoke Organization in Advanced Material Circulation Techniques

In fiscal year of 2021, "Advanced Research Infrastructure for Materials and Nanotechnology in Japan" program supported by Ministry of Education, Culture, Sports, Science and Technology (MEXT) just started, succeeding to MEXT Nanotechnology Platform program that will be finished in 2021. In this new program, six Hub&Spoke teams are constructed with the Center Hub of National Institute of Materials Science (NIMS), and IMS belongs to the Hub&Spoke team of Advanced Material Circulation Techniques with NIMS (Hub), Nagoya Institute of Technology (Spoke), and The University of Electro-Communications (Spoke). Domestic and international equipment sharing is a most important purpose in this program as in the Nanotechnology Platform program. Moreover, users and staffs are requested to provide experimentally obtained data to the Data Platform that are being constructed in NIMS. The accumulated data will be open to all researchers for future material scientific investigations. Human resource development is also an important aim in this program. In IMS, this program is mainly managed by Instrument Center, supported by Research Center for Computational Science in data storage and transfer to NIMS Data Platform. Although practical executions start from next fiscal year, similar equipment sharing will be conducted as in the Nanotechnology Platform program. In 2021, a new electron spin resonance system will be installed through the program. We hope that this program will successfully be performed and equipment sharing usage in IMS will further be accelerated.

Joint Studies Programs

As one of the important functions of an inter-university research institute, IMS facilitates joint studies programs for which funds are available to cover the costs of research expenses as well as the travel and accommodation expenses of individuals. Proposals from domestic scientists are reviewed and selected by an interuniversity committee.

(1) Special Projects

(a) Construction of Synthetic Microdomains to Artificially Assemble Biological Polymers on Lipid Membranes Using Metal Complex Lipids

OHTANI, Ryo (*Kyushu Univ.*)
KAWANO, Kenichi (*Kyoto Univ.*)
KINOSHITA, Masanao (*Kyushu Univ.*)
YANAKA, Saeko (*IMS*)
KATO, Koichi (*IMS*)

Cell membranes are nonuniform entities characterized by heterogeneous molecular assemblies that mediate biological processes exemplified by signal transduction. Accumulating evidence has indicated that these microdomains comprise various lipid molecules including glycosphingolipids and cholesterol and serve as molecular platforms where specific biomolecules accumulate to perform sophisticated functions. To gain a deeper understanding of these complex membrane functions, we employed a multilateral approach in an attempt to artificially control membrane properties and their molecular assembly.

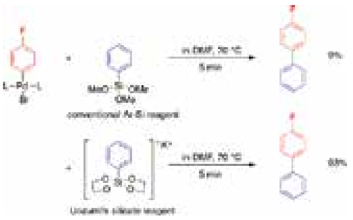
In this project, we created and applied *metal complex lipids* for (1) manipulating lipid membrane properties such as curvature and viscosity to construct synthetic domain architectures and (2) controlling assemblies of biological polymers thereon. The metal complex lipid consists of a metal complex moiety as its hydrophilic head and an alkyl chain as its hydrophobic tail. It exhibits different physical properties from those of natural lipid species, which further impacts lipid membrane properties. Through investigation of the influence of the metal complex lipids on phase-transition and molecular-assembling behaviors of both artificial and cell membranes, we successfully constructed an artificial phase separation system with micro-sized rigid domains consisting of metal complexes in living cell membranes. Furthermore, we succeeded in synthesizing a new metal complex lipid which could provide unique fluid–fluid phase separation in lipid membranes. The metal complex lipid not only exhibits such domain formation property but also offers a possibility to hybridize with biomolecules via the click chemistry approach due the head part incorporating an ethynyl substituent. We expect that this metal complex lipid will be applicable to assembling and accumulating biomolecules in lipid membranes, which is now underway.

We held a collaboration meeting in 2020 to extensively discuss our research progress and future planning. The meeting was held at on-line on July 29th, 2020. This project has achieved two published papers (R. Ohtani *et al. Angew. Chem., Int. Ed.* **61**, 13603–13608 (2021), R. Ohtani *et al. Angew. Chem., Int. Ed.* **59**, 17931–17937 (2020)).

(b) *Operando* Structural Studies on the Reacting Species of the Cross-Coupling Catalysis

FUJIKAWA, Shigenori (*Kyushu Univ.*)
TAKAYA, Hikaru (*Kyoto Univ. and IMS (cross appointment)*)
NAGASAKA, Masanari (*IMS*)
OKUMURA, Shintaro (*IMS*)
UOZUMI, Yasuhiro (*IMS*)

The palladium-catalyzed cross-coupling reactions have been recognized as the most powerful synthetic means of carbon–carbon bond formation. Coupling of aryl halides and organosilicon reagents, the so-called Hiyama coupling, is one of the representatives. Recently, Uozumi at IMS developed aryl silicate reagents which exhibited remarkably high reactivity toward the Hiyama coupling with aryl halides (Scheme 1). These observations prompted us to examine the operando structural studies on the aryl silicates as well as conventional aryl silyl reagents under the actual coupling reaction conditions by *in situ* NEXAFS measurements. For the preliminary measurements, the electronic structures of phenyl groups in



Scheme 1. The Hiyama Coupling Reactions with Uozumi's Aryl Silicate.

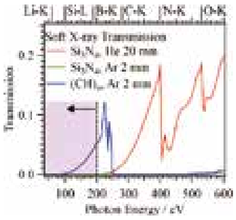


Figure 1. Calculated soft X-ray transmission at several conditions of liquid cells.

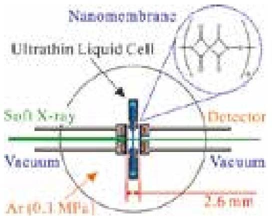


Figure 2. The schematic of an ultrathin liquid cell including Si-free nanomembranes.

organosilicon compounds were investigated by C K-edge NEXAFS (280 eV) at BL3U of UVSOR-III (by Nagasaka, Okumura). From the soft X-ray transmission calculations (Figure 1), on the other hand, the Si L-edge NEXAFS (100 eV) needs the ~2 mm optical length of argon gas and Si-free nanomembranes. Thus, this project combines (1) a new coupling reaction (by Uozumi, Okumura) and (2) an ultrathin liquid cell that achieves the 2.6 mm optical length of argon gas (by Nagasaka, Takaya) including novel Si-free nanomembranes developed by Fujikawa at Kyusyu University (Figure 2) at once to realize the *operando* structural studies of the highly reactive Hiyama coupling reaction. Though, in 2021, this project team have never had the on-site collaborations because of the COVID catastrophe, we have prepared the reacting reagents, Si-free nanomembranes, and an ultrathin liquid NEXAFS cell at each site. This *in situ* NEXAFS method will pave the way for studying various organic reaction with organosilicon, organolithiums, organoboranes, and so on.

(2) Research Symposia

(From Oct. 2020 to Sep. 2021)

Dates	Theme	Chair
Oct. 28–29, 2020	Next Generation Spectro-Mircroscopy and Micro-Spetroscopy Workshop	**OHIGASHI, Takuji**
Dec. 4– 5, 2020	New Development of Molecular Manipulation and Reaction Control Interwoven by Nanospace and Light	**MINAMIMOTO, Hiro** **OKAMOTO, Hiromi**
Mar. 11–12, 2021	The Potential for Academic Development Originating in Coordination Chemistry	**MATSUDA, Ryotaro** **KUSAMOTO, Tetsuro**
Jul. 12–13, 2021	IMS-FHI Symposium “Emerging Techniques of Scanning Probe Microscopy”	**KUMAGAI, Takashi**
Aug. 31, 2021	The Morino Discussion 2021	**MUNAKATA, Toshiaki** **SUGIMOTO, Toshiki**
Aug. 16–19, 2021	The 60th Summer School of Molecular Science by Young Scientistse	**TOKITA, Tsukasa** **SUGIMOTO, Toshiki**

(3) Numbers of Joint Studies Programs

Categories		Oct. 2020–Mar. 2021		Apr. 2021–Sep. 2021			Total			
		Regular	NanoPlat	Regular	NanoPlat	NMRPlat	Regular	NanoPlat	NMRPlat	Sum
Special Projects		1		1			2			2
Research Symposia		3		2			5			5
Research Symposia for Young Researchers		0		2			2			2
Cooperative Research		30	27	20	30	3	50	57	3	110
Use of Facility	Instrument Center		74		69		0	143		143
	Equipment Development Center	1	5	0	5		1	10		11
Use of UVSOR Facility		15	1	101	1		116	2		118
Use of Facility Program of the Computer Center							271*			271*

* from April 2020 to March 2021

Collaboration Programs

(1) MOU Partnership Institutions

IMS has concluded academic exchange agreements with overseas institutions.

The agreements encourage

- Exchange of researchers
- Internship of students and postdoctoral fellows
- Joint research workshops
- Joint research laboratories

Institution	Period	Accept*	Send*
The Korean Chemical Society, Physical Chemistry Division [Korea]	2006.12–2022.10	0	0
Institute of Atomic and Molecular Sciences (IAMS) [Taiwan]	2005. 1–2023. 1	0	0
École Nationale Supérieure de Chimie de Paris (ENSCP) [France]	2009.10–2024.10	0	0
Freie Universität Berlin (FUB) [Germany]	2013. 6–2022. 6	0	0
National Nanotechnology Center, National Science and Technology Development Agency (NANOTEC/NSTDA) [Thailand]	2017.10–2022.10	0	0
Sungkyunkwan University, Department of Chemistry (SKKU) [Korea]	2018. 4–2022. 3	0	0
University of Oulu [Finland]	2021. 5–2024. 5	0	0
National Yang Ming Chiao Tung University [Taiwan]	2018. 6–2023. 5	0	0
Peter Grünberg Institute, Forschungszentrum Jülich GmbH (FZJ) [Germany]	2018.10–2023. 9	0	0
State Key Laboratory of Physical Chemistry of Solid Surfaces (Xiamen University) [China]	2019.12–2024.12	0	0
Indian Institute of Technology Kanpur [India]	2020. 4–2025. 3	0	0
Fritz-Haber-Institut der Max-Planck-Gesellschaft [Germany]	2021. 4–2023. 3	0	1

* No. of researchers during the period from Sep. 2020 to Aug. 2021

Academic Exchange Agreement with Overseas Universities/Institutes (SOKENDAI) as follows ;

Institution	Period	Accept*	Send*
Kasetsart University, Faculty of Science [Thailand]	2011. 3–2021. 4	0	0
University of Malaya, Faculty of Science [Malaysia]	2014. 3–2024.11	0	0
Vidyasirimedhi Institute of Science and Technology [Thailand]	2018. 9–2023. 9	3	0
Friedrich Schiller University Jena [Germany]	2020. 7–2023. 7	0	0

* No. of researchers during the period from Sep. 2020 to Aug. 2021

(2) International and Inter-Institutional Collaboration Symposia

Several international symposia and workshops in molecular science are held in IMS and in Japan. Some workshops are organized with our MOU partners for international collaboration in the MOU partner's country as well as in Japan:

Program	Coordinator	Date	Place
Next Generation Spectro-Microscopy and Micro-Spectroscopy Workshop	MATSUI, Fumihiko (IMS) OHIGASHI, Takuji (IMS)	2020.10.28–29	Online
1st IMS-FHI Symposium “Emerging Techniques of Scanning Probe Microscopy”	KUMAGAI, Takashi (IMS)	2021.7.21	Online

(3) IMS International Internship Program

Category	Number of People	
	Overseas	Domestic
IMS International Internship Program (IMS-IIP)	3*	–

* from Sep. 2020 to Aug. 2021

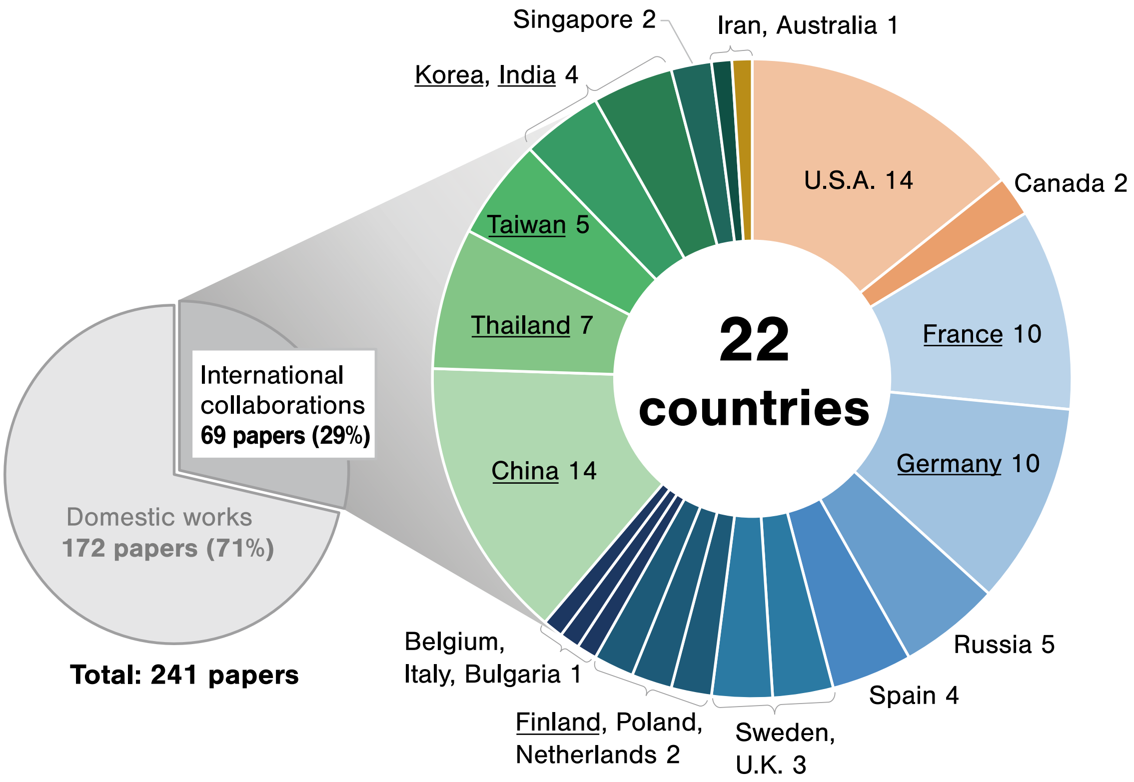
(4) IMS International Collaboration (Including online meetings)

Category	Number of People
International Joint Research Programs	79
International Use of Facilities Programs	14

from Sep. 2020 to Aug. 2021

Internationally Collaborated Publications

Articles and reviews published in 2020



Underlined countries include MOU Partnership Institutions
Scopus dataset, Nov. 2021

AWARDS

FUJITA, Makoto Division of Advanced Molecular Science	Clarivate Citation Laureate 2020 “For Advances in Supramolecular Chemistry through Self-Assembly Strategies that Take Inspiration from Nature Itself”
FUJITA, Makoto MITSUHASHI, Takaaki Division of Advanced Molecular Science	“Major Results” of Nanotechnology Platform “Short and Unified Chemo-Enzymatic Synthesis of Spiroketals, and the Structural Elucidation by the Crystalline Sponge Method”
ISHIZAKI, Akihito Theoretical and Computational Molecular Science	Research Award of Quantum Life Science Society “Development of Fundamental Theory to Describe Dynamical Processes in Open Quantum Systems and Elucidation of Energy Transport and Conversion Processes in Photoexcited Biological Reaction Systems”
HIRAMOTO, Masahiro Materials Molecular Science	Outstanding Achievement Award, Molecular Electronics and Bioelectronics Division, Japan Society of Applied Physics
MINAMITANI, Emi Theoretical and Computational Molecular Science	The 1st Award for Early Career Women Scientists of the Japan Society of Vacuum and Surface Science “Theoretical Study on Quantum Many-Body Effects at Surfaces and Interfaces” The 2nd Fumiko Yonezawa Memorial Prize of the Physical Society of Japan “Computational Study of Nanoscale Magnetism and Phonon”
TAIRA, Yoshitaka UVSOR Synchrotron Facility	The Outstanding Presentation Award of the 64th Annual Meeting of the Japanese Society of Radiation Chemistry “Development of Gamma-Ray Induced Positron Annihilation Spectroscopy at UVSOR-III”
KURAMOCHI, Hikaru Research Center of Integrative Molecular Systems	The 13th Young Scientist Awards of the Japan Society for Molecular Science “Study on the Femtosecond Structural Dynamics of Complex Molecular Systems by Extreme Time-Domain Raman Spectroscopy Using Few-Cycle Pulses” The 13th Inoue Science Research Award “Development and Application of Ultrafast Multi-Dimensional Spectroscopy for Visualizing Reaction Coordinates of the Condensed-Phase Molecules”
MATSUI, Fumihiko UVSOR Synchrotron Facility	NAGAI Foundation for Science & Technology Encouragement Award “Development of Micro Area Analysis Method of Material Surfaces with Unique Electronic Properties by the Momentum Microscope”
SHITADE, Atsuo Theoretical and Computational Molecular Science	Young Scientist Award of the Physical Society of Japan, 2021 “Theoretical Study on Cross-Correlated Responses in Crystals Based on Electronic Multipole”
MIWA, Kuniyuki Theoretical and Computational Molecular Science	Young Scientist Award of the Physical Society of Japan, 2021 “Theoretical Studies on the Optical and Transport Properties of Molecular Systems at the Nanoscale”
KOITAYA, Takanori Materials Molecular Science	The 2021 Vacuum and Surface Science Journal Award of the Japan Society of Vacuum and Surface Science “Surface Chemistry of Carbon Dioxide on Copper Model Catalysts Studied by Ambient-Pressure X-ray Photoelectron Spectroscopy”
IZAWA, Seiichiro Materials Molecular Science	The Young Scientist Award, Molecular Electronics and Bio Electronics Division in the Japan Society of Applied Physics “Exploring Photoelectric Conversion at Organic Semiconductor Interfaces” Konica Minolta Imaging Science Encouragement Award “Novel Photon Up-Conversion for Low Energy Light Utilization” The Outstanding Presentation Award of the 31st Japan OLED Forum “Photon Upconversion via Spin Inversion at Organic Semiconductor Interface”

AWARDS

YAGI-UTSUMI, Maho Life and Coordination-Complex Molecular Science	The 10th Young Scientist Award of National Institutes of Natural Sciences “Molecular Assemblies of Amyloidogenic Proteins”
YANAKA, Saeko Life and Coordination-Complex Molecular Science	Award for Young Scientists by the Division of Physical Sciences of the Pharmaceutical Society of Japan, 2021 “Development of Method for Studying Dynamical Structures and Interactions of Antibodies and Its Applications to Antibody Engineering”
KOSUGI, Takahiro Research Center of Integrative Molecular Systems	Young Scientist Excellence Award of the Protein Science Society of Japan 2021 “De Novo Design of Allosteric Sites into Rotary Motor V_1-ATPase by Restoring Lost Function”
NAKAMURA, Eiken UVSOR Synchrotron Facility	The Chemical Society of Japan Award for Technical Achievements for 2020 “The Development of UVSOR Beamlines and their Related Experimental Apparatuses for Promoting Molecular Science” The Commendation for Science and Technology by the Minister of Education, Culture, Sports, Science and Technology Outstanding Support for Research Award “Development of an L-Shaped Slit for Synchrotron Radiation and Its Contribution to a Design for Beamlines with Insertion Light Sources”

LIST OF VISITING FOREIGN SCHOLARS

Visitors from abroad are always welcome at IMS and they have always played an important role in the research activities of the Institute. The foreign scientists who visited IMS during the past year (September 2020–August 2021) are listed below.

(1) IMS Visiting Scientist

Mr. KUMSAMPAO, Jakkapan	VISTEC	Thailand	Oct. ’19–Sep. ’20
Ms. PACHARIYANGKUN, Anna	VISTEC	Thailand	Nov. ’20–Jul. ’20
Mr. CHAIWAI, Chaiyon	VISTEC	Thailand	Dec. ’20–Nov. ’20

(2) Visitor to IMS

Mr. HOOD, Ken	FusionX Ventures	U.S.A.	Nov. ’20

LIST OF PUBLICATIONS

Theoretical and Computational Molecular Science

Y.-W. KUO, P.-H. TANG, H. WANG, T.-M. WU and S. SAITO, "Tetrahedral Structure of Supercooled Water at Ambient Pressure and Its Influence on Dynamic Relaxation: Comparative Study of Water Models," *J. Mol. Liq.* **341**, 117269 (2021).

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H. KOSHIDA, H. OKUYAMA, S. HATTA, T. ARUGA and E. MINAMITANI, "Effect of Local Geometry on Magnetic Property of Nitric Oxide on Au(110)-(1×2)," *Phys. Rev. B* **103(15)**, 155412 (8 pages) (2021). DOI: 10.1103/PhysRevB.103.155412

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A. SHITADE and Y. ARAKI,, "Magnetization Energy Current in the Axial Magnetic Effect," *Phys. Rev. B* **103(15)**, 155202 (8 pages) (2021). DOI: 10.1103/PhysRevB.103.155202

A. DAIDO, A. SHITADE and Y. YANASE, "Thermodynamic Approach to Electric Quadrupole Moments," *Phys. Rev. B* **102(23)**, 235149 (12 pages) (2020). DOI: 10.1103/PhysRevB.102.235149

Y. FUJIHASHI and A. ISHIZAKI, "Achieving Two-Dimensional Optical Spectroscopy with Temporal and Spectral Resolution Using Quantum Entangled Three Photons," *J. Chem. Phys.* **155(4)**, 44101 (13 pages) (2021). DOI: 10.1063/5.0056808

A. ISHIZAKI and G. R. FLEMING, "Insights into Photosynthetic Energy Transfer Gained from Free-Energy Structure: Coherent Transport, Incoherent Hopping, and Vibrational Assistance Revisited," *J. Phys. Chem. B* **125(13)**, 3286–3295 (2021). DOI: 10.1021/acs.jpcb.0c09847

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Y. PATHAK, K. S. JUNEJA, G. VARMA, M. EHARA and U. DEVA PRIYAKUMAR, "Deep Learning Enabled Inorganic Material Generator (DING)," *Phys. Chem. Chem. Phys.* **22**, 26935–26943 (2020).

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M. LI, Y. ZHAO, K. YUAN, Y. HAN, J. ZHANG, Y. WU, M. EHARA, S. NAGASE and X. ZHAO, "Lithium-Bromine Exchange Reaction on C_{60}: First Theoretical Proposal of Stable Singlet Fullerene Carbene without Heteroatom," *Org. Chem. Front.* **8**, 1551–1562 (2021).

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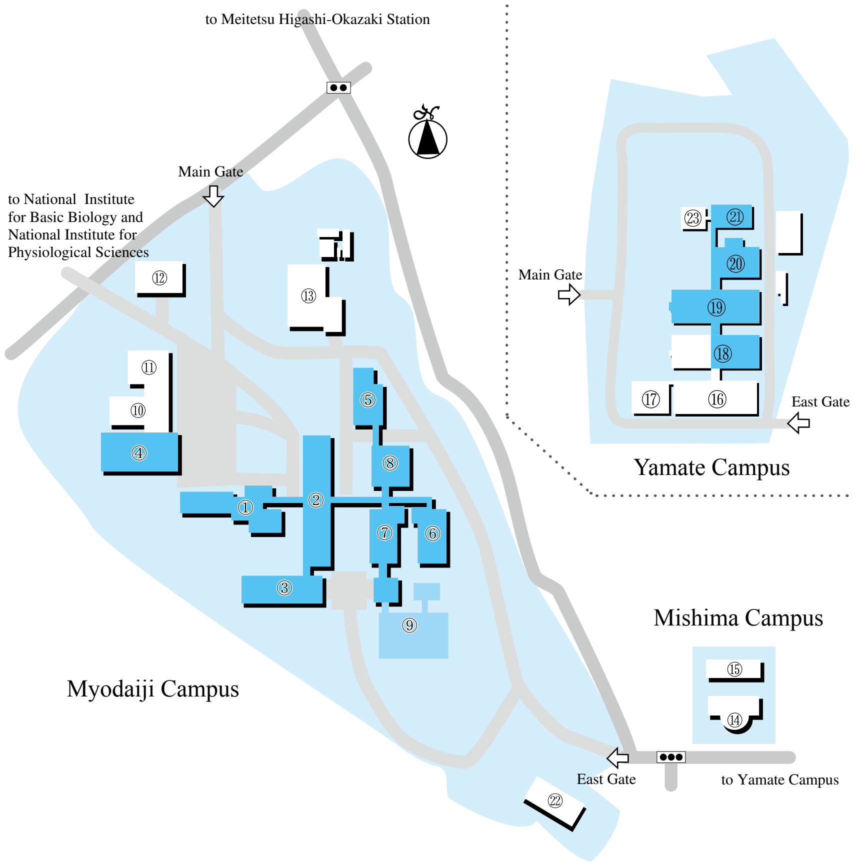
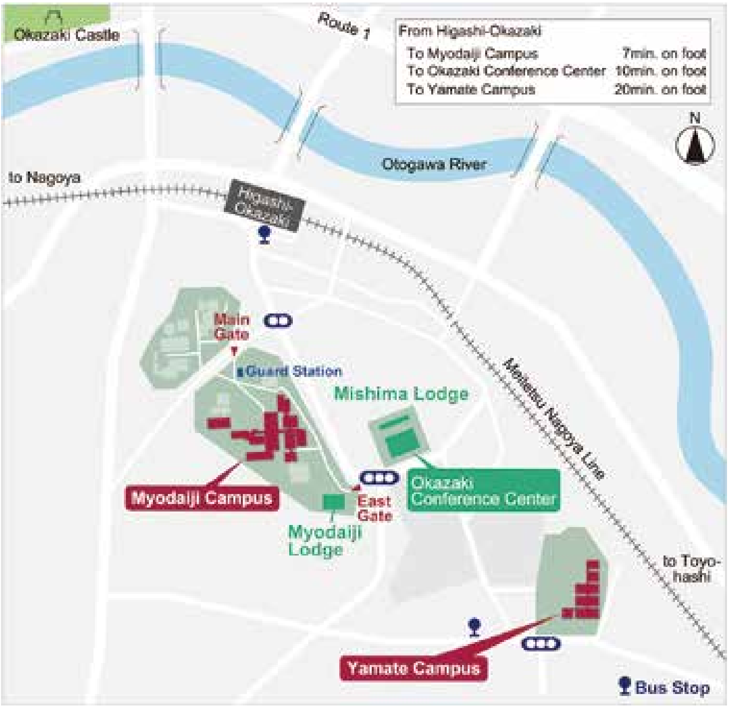
INDEX

to “Research Activities”

MAPS



1. Main Office Bldg.
2. Main Laboratory Bldg.
3. South Laboratory Bldg.
4. Computer Center Bldg.
5. Joint Research Bldg. A
6. Joint Research Bldg. D
7. Joint Research Bldg. C
8. Joint Research Bldg. B
9. Joint Research Bldg. UVSOR
10. Administration Bureau
11. Library
12. Faculty Club & Coop
13. Electricity Control Station
14. Okazaki Conference Center
15. Mishima Lodge
16. Yamate No.1 Bldg. A
17. Yamate No.1 Bldg. B
18. Yamate No.2 Bldg.
19. Yamate No.3 Bldg.
20. Yamate No.4 Bldg.
21. Yamate No.5 Bldg.
22. Myodaiji Lodge
23. NIBB Center of Interuniversity Bio-Backup Project



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To Okazaki Conference Center	10min. on foot
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